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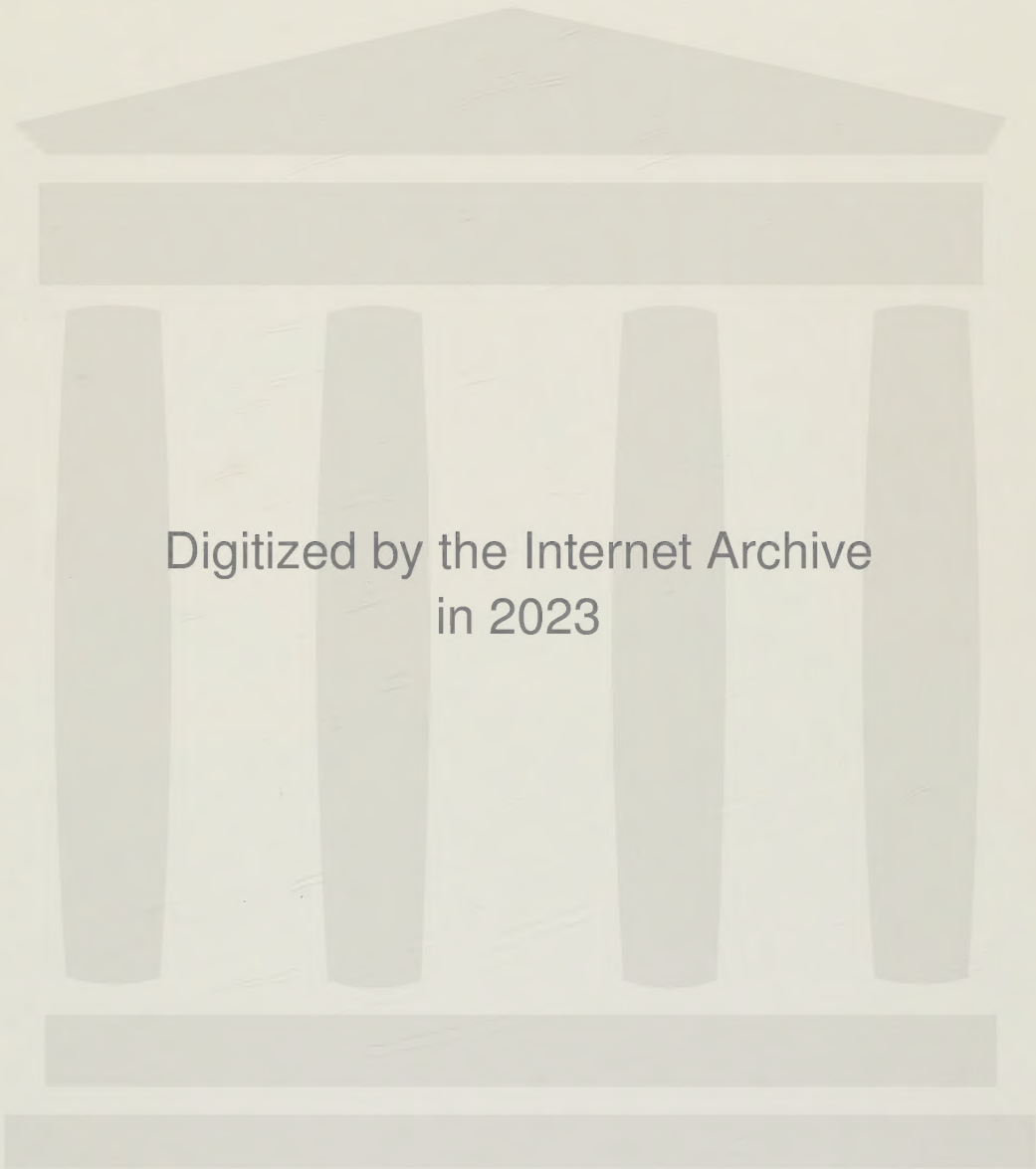

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CHEMICAL PROCESS REVIEW No. 20

Hydrogen Peroxide Manufacture

Dr. Robert Powell

ndc

CHEMICAL PROCESS REVIEWS

Chemical Process Reviews are a series of comprehensive up-to-date chemical engineering studies of a particular and well defined area within the overall chemical process and allied industries. In many cases they are industry surveys in themselves. They are written from the *practical processing point of view*, and are of prime interest to managerial, research, development, marketing personnel, etc., in the process industries. Each Review points out economic considerations where pertinent. Each Review includes a considerable number of illustrations.

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Hydrogen Peroxide Manufacture

1968

Dr. Robert Powell

Thirty Five Dollars

NOYES DEVELOPMENT CORPORATION

PARK RIDGE, NEW JERSEY, U. S. A. LONDON, W.1. ENGLAND

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FOREWORD

Chemical Process Reviews are a series of comprehensive up-to-date chemical engineering studies of a particular and well defined area within the overall chemical process and allied industries. In many cases they are industry surveys in themselves. They are written from the practical processing point of view, and are of prime interest to managerial, research, engineering, development, marketing personnel, etc., in the process industries. Each Review points out economic considerations where pertinent. Each Review includes a considerable number of illustrations.

Chemical Process Reviews are based primarily on the patent literature, supplemented by other commercial information and data, to present a complete picture. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from the patent literature is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure".

These Reviews are bound in paper in order to close the time gap between "manuscript" and "complete book". Industrial technology is progressing so rapidly, that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

This book is organized in such a way that the Table of Contents also serves as the Index.

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GENERAL CONSIDERATIONS

Hydrogen peroxide, a versatile industrial chemical which is rapidly increasing in scale of manufacture and use, has gained commercial status especially since about 1925, when electrolytic processes were introduced into the USA and bleaching uses became important. More recently, cheaper nonelectrolytic processes have been used to expand production, and its use as a rocket fuel in military applications has boosted demand appreciably.

PROPERTIES

Pure hydrogen peroxide, at normal temperatures, is a water-white viscous liquid with the following physical characteristics:

Molecular weight	34.02
Specific gravity	1.438
Melting point	-0.461°C.
Boiling point	155.5°C.

Hydrogen peroxide is miscible with water in all proportions; it is soluble in ether, insoluble in hydrocarbons.

In commercial use it is known only as a solution, and is sold in grades ranging from 3 to 98% concentration. The major grades are 35, 50, 70 and 90% H_2O_2. Hydrogen peroxide is stable in pure form, but in the presence of even traces of metallic impurities it decomposes, often violently:

$$H_2O_2 \longrightarrow H_2O + 1/2\, O_2$$

USES

The largest use of hydrogen peroxide is in the bleaching of cotton textiles. The second largest use is in the oxidation of organic compounds; many organic peroxides are made from H_2O_2. Advances are expected in the usage of H_2O_2 in the following fields: epoxidation of organic compounds (i.e., the addition of an O to the olefinic linkage), the manufacture of peroxy catalysts for polymerization reactions, oxidation of organic

compounds, the use of H_2O_2 as a blowing agent (catalytic release of O_2, e.g., to make foam rubber), and as a source of energy in both military and civilian use. Because of security restrictions, little is known about demand trends in military uses (79) (80).

Other uses of H_2O_2 are medicinal – it has mild bactericidal properties – and in cosmetics (74).

The overall U.S. use pattern (excluding military) according to industry is presently estimated to be as follows:

	Percent
Textiles	40
Pulp and paper	15
Chemical manufacture	25
Miscellaneous	20
	100

ECONOMIC ASPECTS

From 1950 to 1967 U.S. production has increased more than five times, from about 10,000 tons to about 57,000 tons (100% H_2O_2 basis). About 30-35% of this output is used captively. U.S. demand in 1970 is estimated at 65,000-70,000 tons.

MANUFACTURE

There are two main types of manufacturing process for H_2O_2, chemical and electrolytic. In the latter process, sulfate is oxidized to peroxysulfate at the anode of an electrolysis cell. The peroxysulfate produced is subsequently hydrolyzed to give hydrogen peroxide and sulfate which is recycled.

Within the scope of the present work, we shall be concerned exclusively with the chemical routes to H_2O_2, for the reason that all new plants use the chemical rather than the electrolytic process. It probably will be only a matter of time until the latter is completely displaced (79).

The major chemical process is the so-called anthraquinone process; this will be described in great detail and occupy about half of the book; the second half will be devoted to the purification, concentration and stabilization of H_2O_2, and to other manufacturing processes. The latter include the oxidation of secondary alcohols, such as isopropyl alcohol; and H_2O_2 production from barium peroxide by reaction with sulfuric acid, as follows:

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

$BaSO_4$ is a valuable by-product; BaO_2 is prepared by air roasting of barium oxide:

$$BaO + 1/2\ O_2 \xrightarrow{600°C.} BaO_2$$

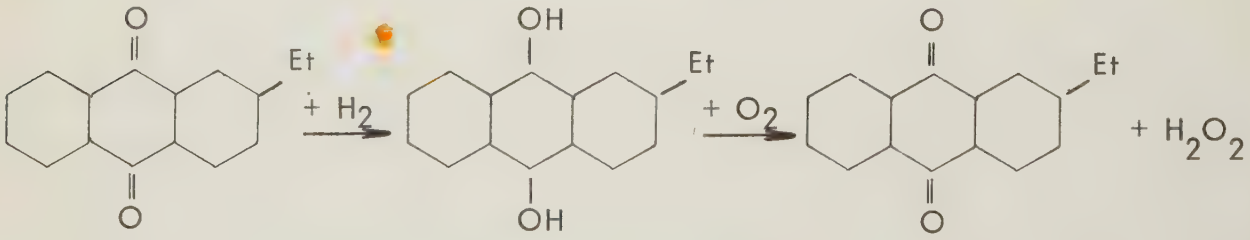
This process was formerly used, but is now of limited interest. However, in Chapter 3, a very recent process is described in which H_2O_2 is produced by reaction of metal peroxide with an organic acid (42).

THE ANTHRAQUINONE PROCESS

INTRODUCTION

The cyclic anthraquinone process for producing hydrogen peroxide, as practiced commercially and as generally described in the literature, involves two main steps which are carried out successively. In the first step, an alkylanthraquinone dissolved in a water-immiscible organic solvent is hydrogenated in the presence of a particulate hydrogenation catalyst, following which the catalyst is separated to yield a solution of the corresponding alkylanthrahydroquinone in the solvent. The latter solution is then oxygenated in the second step by means of air or oxygen to regenerate the solution of the alkylanthraquinone which is recycled to the first step after first separating from the solution the hydrogen peroxide which is simultaneously formed.

In the following equation, the process mechanism has been depicted for 2-ethylanthraquinone as working material:



The hydrogen peroxide can be separated by distillation, but is usually extracted with water. The extraction is normally carried out in a vertical column with aqueous extracting phase moving downwardly countercurrently to an upwardly moving oil phase of the "working solution".

In the above process, the alkylanthraquinone is generally referred to as the "working material", the water-immiscible solvent employed to dissolve it is referred to as the "working solvent", and the solution of the working material in the working solvent is referred to as the "working solution". The term "working material", as commonly employed, may also designate a tetrahydroalkylanthraquinone, a mixture of alkylanthraquinones or tetrahydroalkylanthraquinones, or a mixture of one or more alkylanthraquinones with one or more tetrahydroalkylanthraquinones, all of which effectively produce hydrogen peroxide

when a working solution of these in a working solvent is employed in the cyclic process.

As indicated, any of the alkylanthraquinones, the corresponding tetrahydroalkylanthraquinones and mixtures of two or more such compounds may be employed as working materials. Specific examples of compounds which may be used alone or in mixtures are the 2-ethyl-, 2-isopropyl-, 2-secondary-butyl-, 2-tertiary-butyl-, 1,3-dimethyl-, 2,3-dimethyl-, 1,4-dimethyl-, 2,7-dimethyl-, 2-iso-secondary-amyl- and 2-tertiary-amyl- anthraquinones, and the corresponding tetrahydroanthraquinones. The continued use of a starting alkylanthraquinone usually results in a slow conversion of a part thereof to the corresponding tetrahydroalkylanthraquinone, so that the working material then will consist of a mixture of the two compounds.

The working solvent may be a single solvent or a mixed solvent, containing a constituent for dissolving the quinone form of the working material and a constituent for dissolving the hydroquinone form of the working material. Such solvents are well known in the art. Some of the many solvents that have been used or proposed for use are described in U.S. Patents 2,215,883, 2,537,516, 2,537,655, 2,668,753, 2,768,065, 2,768,066, 2,791,491, 2,890,105, 2,919,974, 2,927,002 (9), 2,975,033 (10), 2,990,251 (11) and 3,002,817 (12).

Hydrogenation catalysts which have been used or proposed for use include Raney nickel and the noble metals, ruthenium, rubidium, platinum, rhodium and palladium. The noble metals are employed on carriers or supports, examples of which are activated alumina, magnesium oxide, titanium oxide, silica-alumina and the like.

The working material of the anthraquinone process is a costly chemical which must be used repeatedly and with little loss in order that the process be economically attractive. It is well known that long continued use of a working solution results in the degradation of a significant proportion of the working material to form products which are inert, i.e., do not produce hydrogen peroxide in the normal cyclic operation of the process. Such inert degradation products represent a substantial cost item, since they must be removed from the working solution and replaced by expensive active working material in order that the H_2O_2-synthesizing capacity of the working solution be maintained at the desired high level.

The formation of degradation products has long been recognized as a major problem associated with the anthraquinone process, and various ways have been proposed for reducing or inhibiting their formation or for reconverting at least some of them to active working materials. Formation of the degradation products appears to arise mainly from the side reactions which take place in the hydrogenation step. One proposal for reducing the formation of such degradation products involved controlling the degree of hydrogenation in the hydrogenation step to not more than 55% of theoretical (Canadian Patent 577,144). Another proposal was to reduce the contact time between the hydrogenation catalyst and the working solution [U.S. Patent 3,009,782 (25)]. Still another proposal was to employ a fixed bed hydrogenation catalyst which is a noble metal on a support material of low surface area and low pore volume [U.S. Patent 3,030,186 (26)]. It has also been proposed to inhibit formation of such degradation products during hydrogenation by having dissolved in the working solution fed to the hydrogenator alkali compounds such as various amines (British Patent 795,272).

The anthraquinone process being a cyclic process, it is important that the working solution has the physical properties, e.g., viscosity and density, which meet the requirements for efficient operation of all steps in the cycle, and that it chemically produces as great a yield of hydrogen peroxide per pass through the cycle as is possible. This latter in turn is dependent upon the solubility of the reaction carrier, or working material, and therefore the proportion of the cycling working solution which represents reactive material.

Several techniques have been proposed for obtaining a high solubility of the working compound; they may be divided into two general approaches. The first approach involves a search for special anthraquinone derivatives, referred to often simply as anthraquinones or substituted anthraquinones, having high solubilities in solvents. Such quinone derivatives include 2-tertiary butylanthraquinone, amylanthraquinones, tetrahydroanthraquinones, mixtures of isopropyl- and secondary-butylanthraquinone, eutectic mixtures of anthraquinones, esters of anthraquinone carboxylic acids and heteronuclearly disubstituted alkylanthraquinones.

The second approach involves use of special solvents or solvent mixtures with selective dissolving abilities for the anthraquinone and/or anthrahydroquinone forms of the working material. The requirements for such solvents to be applied in operating plants are varied and difficult to satisfy, and attempts have been made to satisfy as many requirements as possible by combinations of various solvents.

In general, solvent combinations contain as individual components a solvent particularly effective in dissolving the anthraquinone form, and a solvent particularly effective in dissolving the anthrahydroquinone form. Inert additives sometimes are added to these solvent mixtures to provide properties needed to satisfy particular requirements, such as the need for low viscosities and densities. The low viscosity is important for mechanical reasons in cycling of the working compound through the reaction equipment, and the density must be substantially different from the density of the water-hydrogen peroxide solution resulting from water extraction of the hydrogen peroxide from the organic working solution, in order to facilitate the extraction.

Several known solvent combinations may be quoted here; in these combinations the solvent for the anthraquinone form is recited first: C_8 to C_{17} ketone or xylene and C_5 to C_{12} alcohol; anisole and heptyl alcohols; benzene or alkyl benzene and methylcyclohexanol acetate; methylnaphthalene, tertiary-butyl toluene or xylene and diisobutylcarbinol; methylnaphthalene and a phosphoric acid ester. While they have been found useful, few, if any, of these particular mixtures or other solvent mixtures employed have satisfied all of the requirements for systems of this kind.

After extraction of the hydrogen peroxide, the working solution is purified with a purifying agent (e.g., aluminum oxide) before being recycled to the hydrogenation stage. The amount of purifying agent which is destroyed during purification depends on the amount of by-products, which are produced almost exclusively in the hydrogenation stage. As a general rule, the amount of by-products is directly proportional to the concentration of hydrogenation catalyst used. This means that a highly active catalyst supplies the least by-products.

Process Costs

Air, water and purifying agent are the raw materials consumed by the reaction to produce hydrogen peroxide. However, losses in working solution resulting from by-product formation, and the relatively high costs for the hydrogenation catalyst, must also be added in a cost calculation. Accordingly, as a practical matter, the following items constitute the principal elements of cost in the process:

Hydrogenation catalyst
Working solution loss due to by-product formation
Consumption of purifying agent
Hydrogen consumption

As would be expected, there have been numerous attempts to reduce these principal costs to a minimum, and numerous patents relate to inventions made as a result of these attempts. These patents can be divided into two groups.

Pretreatment of Catalysts: The first group involves patents in which by-product formation is reduced by subjecting the hydrogenation catalyst to a preliminary treatment. Nitrites (U.S. Patent 2,720,531), nitriles (U.S. Patent 2,720,532), amines (U.S. Patent 2,730,533), and pyridines (U.S. Patent 2,756,243) are proposed for pretreatment. Pretreatment agents for the most part are alkaline, nitrogen-containing substances. At the former BASF plant, as has been described in numerous BIOS, CIOS, and FIAT reports, water-soluble alkaline-reacting ammonium salts were used for pretreatment of the hydrogenation catalyst. It is common to all processes of the first group that the catalyst is made more selective by the pretreatment, and thus by-product formation is reduced. However, a quite considerable reduction in activity of the hydrogenation catalyst is also linked to the pretreatment, so that overall catalyst costs rise considerably.

Additives to Working Solution: The second group of patents cover processes in which it is recommended to add to the working solution, substances causing a reduction in by-product formation. German Patent 1,041,928 recommends the addition of chlorine-containing compounds in order to direct hydrogenation in a desired direction. It is recommended in British Patent 795,272 that organic nitrogen-containing substances be added to the working solution. It is stated that these compounds should be as water-insoluble as possible, or their water solubility at 25°C. should not amount to more than two grams per liter, since they would otherwise be washed out in the extraction stage.

In comparison with the first group of processes, the second group also has the advantage of reducing the amount of by-products; however, when the organic nitrogen-containing compound is added to the working solution, as in British Patent 795,272, the activity of the hydrogenation catalysts remain substantially unchanged.

WORKING MATERIALS

In the anthraquinone process, the hydrogenation of one mol of the quinone form of the working material theoretically produces one mol of the hydroquinone form. When this is

oxidized, it theoretically yields one mol of hydrogen peroxide intermixed with the original mol of the working material in its quinone form. Upon water extraction, a mol of hydrogen peroxide is obtained as product, with the original mol of working material in its quinone form being returned to the working solution. Accordingly, the amount and concentration of peroxide obtained depends upon the mols of working compound which are alternately reduced and oxidized per pass through the equipment.

Therefore, in order to carry out this process commercially, enough anthraquinone working compound must be dissolved in the working solution so that practical yields of hydrogen peroxide are obtained per pass of working solution through the system. An increase in the solubility of the working compound in the working solvent, proportionally increases the hydrogen peroxide content which is released in the working solution and which subsequently can be extracted. With this relationship in mind, the prior art has chosen two separate and distinct methods for increasing the solubility of the anthraquinone working compounds in the working solutions.

The first group makes use of special solvents, or solvent mixtures, with preferred solution power for various anthraquinone compounds. Among the solvents which are employed are hydrocarbons, alcohols, ketones, carboxylic acid esters, phosphoric acid esters, ethers, and others. More specific processes employing improved solvents, or solvent mixtures, are taught in German Patent 942,807 and U.S. Patents 2,537,516, 2,537,655 and 2,668,753.

The second group increases the amount of working material dissolved in a unit quantity of working solution by employing special anthraquinone derivatives with preferred higher solubilities. Thus, in place of the conventionally employed 2-ethylanthraquinone, U.S. Patent 2,689,169 teaches a working material having even greater solubility, namely, 2-tert-butylanthraquinone. Other compounds, such as hetero nuclear disubstituted alkyl-anthraquinones taught in German Patent 1,051,257, exhibit a very high solubility as well as a high stability against over-hydrogenation. Compounds, such as anthraquinone-2-sulfonic acid taught in British Patent 803,121, have been suggested as working materials because of their increased solubility.

On the next few pages, in this section, other novel working materials proposed will be discussed.

Eutectic Mixtures of Alkylated Anthraquinones Are Considerably More Soluble than Single Alkylated Anthraquinones

FMC; Darbee, L.R., and Kreuz, D.F. (1): In the manufacture of hydrogen peroxide by the anthraquinone process, attempts have been made so far to increase the amount of working material present in the equipment and in solution by providing a mixed solvent, one constituent of which possessed exceptional solvent power for the hydroquinone form of the working material, and another constituent of which possessed exceptional solvent power for the quinone form of the working material. This type of operation is exemplified by the disclosure contained in U.S. Patents 2,158,525 and 2,215,883, the commercial operation being set forth in Publications Board Report 4336, U.S. Dept. of Commerce, Washington, D.C.

As was stated before, from the theoretical point of view, one mol of hydrogen peroxide can be produced from one mol of alkylated anthraquinone, providing the alkylated anthraquinone, the working material, is completely hydrogenated. In normal practice, the hydrogenation is not carried to 100% by reason of certain undesirable side reactions which may occur, but is normally carried to only about 50%. (See PB Report 4336.)

Additional suggestions for increasing the amount of hydrogen peroxide obtainable from an alkylated anthraquinone rest upon an increase in the solubility of the working compound in a given amount of working solution; to this end it has been suggested to employ one of the allegedly more soluble alkylated anthraquinones, namely tertiary butylanthraquinone, all as set forth in U.S. Patent 2,689,169.

From the above it will be seen that it is highly desirable to increase the amount of working material present in a given volume of working solution or passing through a particular equipment in which this cyclic operation is conducted in any given unit of time and, furthermore, to be able to increase the degree of hydrogenation permitted.

These objects and other advantages are obtained by employing as the working material in the cyclic hydrogenation and oxidation of alkylated anthraquinones and their tetrahydro derivatives, special and limited mixtures of alkylanthraquinones which possess maximum solubility in the usual solvents employed in the anthraquinone process. To this end, specific compositions of mixtures of alkylated anthraquinones in the neighborhood of the eutectic mixtures in binary, tertiary and quaternary systems are employed as the working material, since by this means it is possible to obtain in solution, in a given solvent, as much as several times the amount of working compound as may be carried in solution when a single alkylated anthraquinone is used as the working material or when random mixtures of these are employed.

Employing a mixed solvent of 40 cc. of anisole and 60 cc. isoheptyl alcohol, 15 grams of 2-ethylanthraquinone may be carried as working material with production of approximately 1 gram of hydrogen peroxide on hydrogenation with 800 cc. of hydrogen. In contrast to this, a eutectic mixture of 2-secondary butylanthraquinone and 2-ethylanthraquinone, that is, a composition of the lowest melting point of those two components consisting of 73.5% 2-secondary butylanthraquinone and 26.5% 2-ethylanthraquinone, dissolve in a similar solvent to well over twice the extent of the single alkylanthraquinone, 2-ethylanthraquinone.

It may further be pointed out that 2-ethylanthraquinone at 20°C. is soluble in trioctylphosphate to the extent of 1.5 grams in 100 cc. of trioctylphosphate. The eutectic composition, 73.5% 2-secondary butylanthraquinone, 26.5% 2-ethylanthraquinone, however, is soluble to the extent of 47 grams per hundred cc. of that solvent, an increase of over 3,000%. At 40°C. the comparison is even more striking, 2-ethylanthraquinone at that temperature being soluble to the extent of 50 grams per 100 cc. of solvent, the eutectic mixture being soluble to the extent of 260 grams per 100 cc. of trioctylphosphate. It will be readily apparent that the increase in solubility will make possible a reduction in the amount of mixed working solution or a reduction in the amount of either or both the solvent for the hydroquinone form of the working material and the solvent for the quinone form of the working material, it being apparent that with a reduction in volume of working solvent

there will be a corresponding increase in working material passing through the equipment in one cycle which is reduced and oxidized. There is, therefore, an increase in the amount of hydrogen peroxide theoretically capable of production in one pass of the working solution, i.e., working solvent and dissolved working material in one cycle.

Figure 2.1 is a graph of the solubility of the system 2-ethylanthraquinone and 2-secondary butylanthraquinone in trioctylphosphate at 40°C., the ordinates being expressed in the number of grams of material soluble in 10 cc. of trioctylphosphate at the indicated temperature, while the abscissa represents compositions in the binary system 2-ethylanthraquinone and 2-secondary butylanthraquinone of from 0 to 100% of each component. The graph shows that whereas a random mixture of 2-ethylanthraquinone and 2-secondary butylanthraquinone of 80% of the former, and 20% of the latter, possess a solubility of about 0.5 gram in 10 cc. trioctylphosphate and a 50/50 mixture, a solubility of 1.75 grams, the 30:70 mixture has increased to about 7.5 grams, the increase in solubility being extremely rapid thereafter to the eutectic mixture, which is soluble to the extent of about 23 grams in 10 cc. trioctylphosphate, comprising 73.5% 2-secondary butylanthraquinone and 26.5% 2-ethylanthraquinone.

Eutectic mixtures of other binary systems are as follows:

44.5% 2-ethylanthraquinone
55.5% 2-tertiary butylanthraquinone
Melting point, 69°C.

31.5% 2-tertiary butylanthraquinone
68.5% 2-secondary butylanthraquinone
Melting point, 43°C.

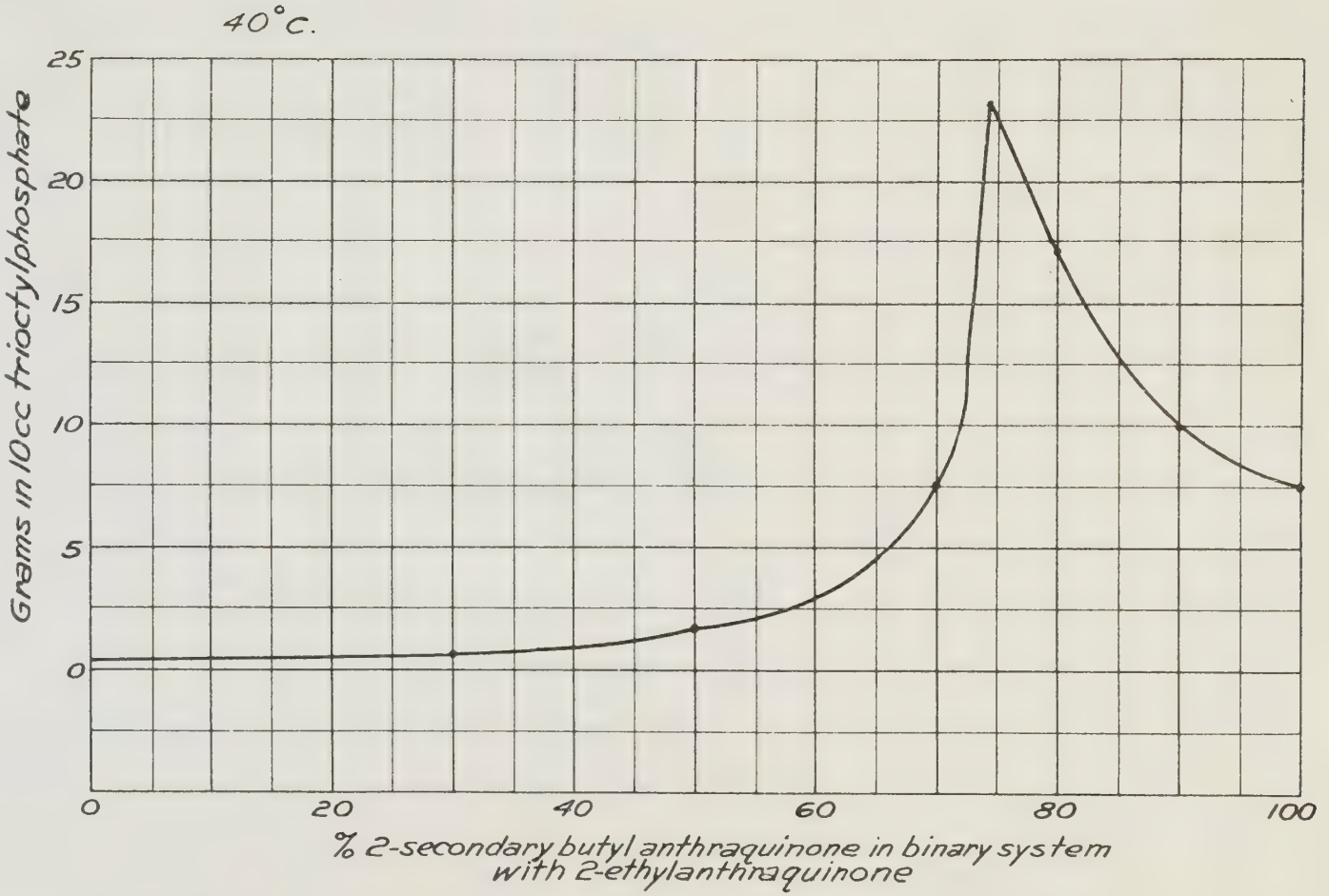
26.5% 2-ethylanthraquinone
73.5% 2-secondary butylanthraquinone
Melting point, 42°C.

The solubility of such eutectic mixtures shows solubility curves similar to that illustrated in Figure 2.1.

In a typical operation of the present process, a liter of solvent consisting of 99% by volume trioctylphosphate and 1% by volume dimethyl naphthalene may be used to dissolve 400 grams of a mixture of 78% secondary butylanthraquinone and 22% 2-ethylanthraquinone, a composition approximating the eutectic mixture of a binary system of those components to produce a working solution, the volume of which is 1.34 liters. This corresponds to 300 grams of working material per liter of working solution. This solution, when hydrogenated to 50% of its capacity of hydrogen take-up to produce hydroquinone, and subsequently oxidized and then extracted with water, produces 19.2 grams hydrogen peroxide per liter of working solution.

This yield of hydrogen peroxide is in contrast to a production of 11.3 grams hydrogen peroxide per liter, as outlined in U.S. Patent 2,768,066, granted October 23, 1956, to Dawsey and Umhoefer, and a yield of 5.5 grams hydrogen peroxide per liter of working solution, as outlined in PB Report 4336.

FIGURE 2.1: SOLUBILITY OF THE SYSTEM 2-ETHYLANTHRAQUINONE AND 2-SECONDARY BUTYLANTHRAQUINONE IN TRIOCTYLPHOSPHATE AT 40°C.



Source: L.R. Darbee, D.F. Kreuz, U.S. Patent 2,966,397, December 27, 1960

In the above example it will be noted that the amount of dimethyl naphthalene, namely the solvent constituent for dissolving the quinone form of the working material, is extremely small; in fact, it may be possible to operate in a single solvent. The larger quantity of working material when reduced requires a solvent for the hydroquinone form, and any of the well known solvents may be used to this end, for instance phosphate esters, phosphonate esters, C_7 to C_{11} aliphatic alcohols, alkyl cyclohexanol, sebacate esters and others. In this anthraquinone process, the makeup and type of solvent used seem of lesser importance than before.

It will be seen from the above that by choosing selected mixtures of the alkylanthraquinones, particularly those mixtures of the alkylanthraquinones having alkyl side chains of from 1 to 4 carbon atoms, which mixtures are the lowest melting point mixtures for that particular system, one may obtain an outstanding advantage in increased solubility of working material content per liter of working solution, thereby to increase materially the yield of hydrogen peroxide per liter of working solution and thus to increase the capacity of a given piece of equipment adapted to be used in the cyclic reduction and oxidation in the so-called anthraquinone process for producing hydrogen peroxide.

Although the solubility of the eutectic mixture has been illustrated and shown in Figure 2.1, it will be apparent that excellent results may be obtained by using as a working material a mixture containing 2-secondary butylanthraquinone and 2-ethylanthraquinone, in which the former is present to the amount of 70% to 85% and the latter, 30% to 15% by weight. As to the system 2-ethylanthraquinone and 2-tertiary butylanthraquinone, extremely advantageous results and yield of hydrogen peroxide, by reason of increased solubility, may be obtained with a working solution of 50 to 30% of the former and 50 to 70% of the latter by weight. In the system 2-secondary butylanthraquinone, 2-tertiary butylanthraquinone, the range of materials will be 65 to 80% of the former and 35 to 20% of the latter by weight.

In an operation where an inhibited catalyst is not employed, nuclear hydrogenation occurs and the amount of the tetrahydro derivatives present may be controlled by subjecting a part or all of the working material to known dehydrogenation procedures to maintain a desired relationship between the original anthraquinones and their tetrahydro derivatives. An initial binary system, in such an event, becomes a quaternary system, which system is operable to produce hydrogen peroxide.

2-Amylanthraquinone Gives High Concentration H_2O_2 Solutions, Obviating the Need for Vacuum Distillation

Dawsey, L.H. (2): The highest strength aqueous product hitherto manufactured directly by any of the anthraquinone autoxidation methods has been a 35% hydrogen peroxide solution (U.S. Patent 2,689,169). Although 50% peroxide has for quite some time been the preferred commercial product, because of savings afforded in shipment, all anthraquinone process product has, until now, required concentration through costly vacuum distillation in order to convert to the preferred article of trade.

An object of the present process is to provide an improved autoxidation process for the direct production of concentrated 50% to 60% aqueous hydrogen peroxide, of high purity, without the need for special vacuum distillation.

The novel working compound of this process is a new organic intermediate, 2-amylanthraquinone, with the empirical formula $C_{19}H_{18}O_2$ and molecular weight of approximately 278. It may consist entirely of one of the eight theoretically possible isomers, or, it may consist of a mixture of isomers, depending upon the spatial arrangement of the five carbon atoms in the amyl-radical attached to the anthraquinone nucleus. Regardless of isomeric composition, the intermediate, when substantially pure, may be characterized physically as a thermally stable, nonvolatile, pale-yellow substance of low melting point and of consistency about like that of castor oil when liquid, with a specific gravity ranging between 1.01 and 1.15, which sets to a glassy solid upon cooling, and which is insoluble in water, but readily soluble in most of the common organic solvents.

The yellow product is not soluble in all proportions with methanol or ethylene glycol, but is much more soluble in ethanol, propanol, etc.; hydrocarbons like mineral oil, kerosene, gasoline, and petroleum ether mix readily; likewise, organic acids, esters, ethers, ketones, amines, and most plasticizers mix easily. The intermediate is completely soluble in concentrated sulfuric acid from which it may be recovered upon dilution with water. It exhibits a broad range of mutual solubility with numerous and diverse solvents, hardly to be expected from a prior knowledge of the properties of other alkylanthraquinones which have been solids and relatively insoluble.

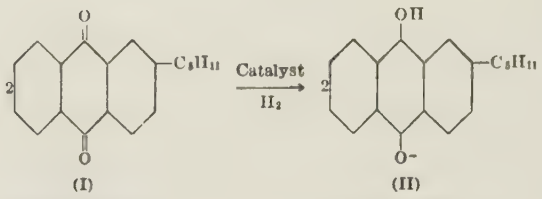
Perhaps, the most outstanding physical distinction for amylanthraquinone is that certain forms may exist as a liquid at ordinary temperatures. Alkylanthraquinones known heretofore have been crystalline solids of considerably higher specific gravity than that shown by the intermediate of this process. Chemically speaking, the intermediate is stable toward oxidizing agents, but changed by reducing agents to the anthrahydroquinone. Upon hydrogenation with active catalyst at elevated temperature, amylanthraquinone can be further reduced to tetrahydroamylanthrahydroquinone. Isolation and purification of the product from organic solutions can be accomplished by vatting with excess sodium dithionite and alkali, filtering off the red aqueous solution to remove foreign matter, and blowing with air. Treatment of amylanthraquinone with oleum at excessive temperatures leads to sulfonation.

When synthesized on a commercial scale, mixtures of the amylanthraquinones may generally be made more economically than the pure individual isomers. Either the purified or the crude intermediate may be utilized for most purposes in making work solutions for the production of hydrogen peroxide by autoxidation methods. The utility of the intermediate of this process is based upon discovery of a successful method for synthesizing the 2-amylanthraquinones. The intermediate has been unknown so far. In no instance have the preparation or the properties been recorded. Although Peters and Rowe (J. Chem. Soc. 1945, 181-182) successfully applied the customary sulfuric acid cyclization to the 2-(4'-alkylbenzoyl)benzoic acids in the synthesis of the corresponding 2-propyl- and 2-butylanthraquinones, they failed in all attempts to produce 2-amylanthraquinone or any other alkylanthraquinone in which the alkyl group contained more than four carbon atoms. The physical existence of only one alkylanthraquinone of molecular weight above that of the butyl-derivative has actually been demonstrated in the past, and this particular substance was 2-n-heptylanthraquinone, of melting point 87°C., prepared by a devious and costly method and recorded several decades ago as a scientific curiosity (J.A.C.S. 55, 2815, 1933). The naming of several hypothetical alkylanthraquinones of higher molecular weight

has been prompted (Harris, U.S. Patent 2,668,753) by the Peters and Rowe publication, but such hypothetical compounds may be presumed nonexistent, especially in the absence of a workable method of synthesis or description of properties.

In accordance with the broad aspects of the process, the production of hydrogen peroxide by means of 2-amylanthraquinone proceeds in two main stages: (1) the hydrogenation stage where the quinone form of the intermediate is reduced to the semiquinone form and (2) the oxidation stage where the semiquinone is oxidized back to the quinone with the splitting off of hydrogen peroxide. The first stage may be characterized by the following specific equation:

(1)

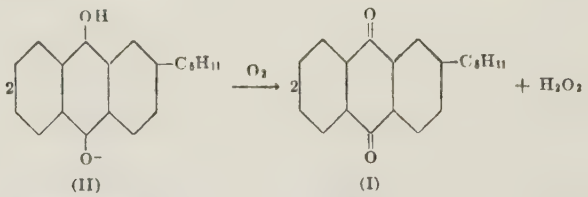


(I) Quinone, yellow, completely soluble

(II) Semiquinone, dark colored, soluble

Hydrogen peroxide is produced by the oxidation of the 2-amylanthrasemiquinone (II) with oxygen in the second stage, as follows:

(2)



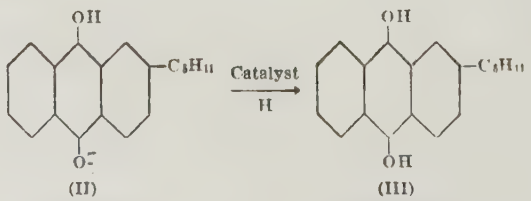
(II) Semiquinone

(I) Quinone

The cycle of the two stages is then repeated after separation of the peroxide from the organic solution, as the original 2-amylanthraquinone (I) is regenerated in stage 2.

The reduction of the semiquinone may also be carried beyond stage 1 illustrated above, by partial or complete hydrogenation to the hydroquinone which may be characterized by the equation:

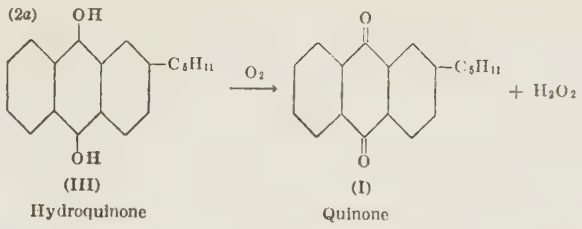
(1a)



(II) Semiquinone, dark colored soluble

(III) Hydroquinone, fluorescent, yellow, less soluble

The hydroquinone (III) is autoxidizable and hydrogen peroxide may also be produced from it in the second stage, as follows:



with regeneration of the original quinone (I) in stage 2a and separation of the hydrogen peroxide formed.

The reduced intermediates may therefore be the 2-amylanthrasemiquinone (II) or the 2-amylanthrahydroquinone (III), or a mixture of these. When hydrogenated beyond the hydroquinone (III) stage, the reduced intermediate may also partially consist of tetrahydro-2-amylanthrahydroquinone, which is likewise oxidizable in accordance with the Equation 2a above.

The 2-amylanthrasemiquinone (II) is about twice as soluble as the hydroquinone (III) in most organic media. Somewhat different reduction principles have applied so far in the hydrogenation of the lower molecular weight alkylated anthraquinones. In the case of the ethyl- and butyl-derivatives, for example, no particular solubility advantages have been noted for the semiquinone forms. In the case of 2-amylanthraquinone, however, the semiquinone shows a decided solubility advantage over the hydroquinone form.

The process may be practiced with all of the various types of solvents used in the past, but since 2-amylanthraquinone is highly soluble in practically all of the common organic solvents, the need for the special so-called "quinone-type-solvents" in the work solution is eliminated. This high solubility coupled with low specific gravity confers a decided advantage in the use of 2-amylanthraquinone. Higher concentrations of the intermediate can be worked, the peroxide production capacity of the solution can be increased, and the direct extraction of concentrated aqueous product may be attained thereby. The compounding of work solutions with 2-amylanthraquinone intermediate may be accomplished with a single solvent or a combination of several types of solvents.

No special quinone type solvent, such as for example benzene, xylene, methyl naphthalene, etc., is necessary, although the latter type may be used for diluent purposes just as other hydrocarbons, like kerosene, might be incorporated in the mixture to adjust some physical property. In the absence of a need for a quinone solvent constituent, the intermediate may be simply blended with one of the so-called "hydroquinone type" solvents. Examples of the latter are methylcyclohexanol and tetradecanol of the alcohol class, or, tributylphosphate and trioctylphosphate in the phosphate ester class, although useful solvents are not necessarily restricted to these classes. Any medium possessing the properties of high semiquinone solvency, mobility, low vapor pressure, chemical stability, water insolubility, etc., may be applicable. It is obvious that diluent solvents may be added for various purposes to the work solution used in the cyclic process.

The following example illustrates the comparatively high productivity afforded by the new intermediate when used in solution with accepted solvents of the past.

A mixture of amylanthraquinones originally derived from cyclization of a 2-(4'-t-amyl-benzoyl)-benzoic acid of melting point 135° to 137°C. was dissolved in hexane, for purification purposes, and filtered at room temperature through a layer of powdered activated alumina. After evaporation of the hexane, the product was a pale yellow viscous oil of specific gravity 1.12, consisting largely of 2-t-amylanthraquinone. This intermediate was compounded into a work solution initially containing, by volume, 26.8% intermediate, 43.2% refined kerosene of specific gravity 0.82 and distillation range 245° to 273°C., and 30% trioctylphosphate. The resulting solution contained 300 grams, or 1.08 mols, per liter intermediate, had a specific gravity of 0.932, and a distribution coefficient of about 45 with 50% aqueous hydrogen peroxide. The distribution coefficient determined was the ratio of peroxide concentration found in the aqueous phase divided by that found in the oil phase after equilibrium was established at 30°C.

The above solution was worked a number of complete cycles which included hydrogenation, oxidation, and extraction of product until part of the anthraquinone intermediate originally added in the work solution had been changed to the tetrahydro-2-amylanthraquinone, as demonstrated by the red color of the solution near the end of the oxidation stage and the longer time required to complete such oxidation. A measured volume of the used solution was then placed in a hydrogenation vessel fitted with an agitator, gas and liquid inlets and outlets, a filter and a meter adapted to measure hydrogen absorption.

After addition of catalyst, the solution was hydrogenated at a temperature of 30°C. until 0.54 mol of hydrogen per liter of solution had been taken up, corresponding to 100% conversion of the intermediate from the quinone stage to the semiquinone stage. During such hydrogenation, the agitated solution was continuously seeded with a small portion of a suspension of crystals, previously prepared by overhydrogenation of part of the same work solution, in order to induce crystallization before filtration. No crystallization occurred. The reduced solution was filtered from the hydrogenation vessel into an oxidation vessel where it was aerated until the original color was restored. The hydrogen peroxide extracted from the work solution with water amounted to 16.5 grams, or 0.49 mol, per liter of the organic solution. The conversion efficiency of hydrogen to the peroxide was 91% during the cycle. The maximum strength of aqueous hydrogen peroxide extractable at equilibrium from the oxidized work solution, calculated from the determined distribution coefficient, was 59% by weight.

This example illustrates a high work capacity and improved product strength made possible through use of 2-amylanthraquinone intermediate. Comparable working of 2-ethylanthraquinone gave only 8.5 grams of H_2O_2 per liter capacity in a similar work solution, with recovery of a 27.5% aqueous product at best (U.S. Patent 2,768,065).

Utilization of Tetrahydroanthrahydroquinone in an Amount Greater than 85% of the Working Material Present Enables High Temperature Operation with Increased H_2O_2 Yields and Reduction in Degradation Products

FMC; Jenney, T.M., and Porter, D.H. (3): The working compounds employed by prior

workers have been found to be commercially desirable because of the relative ease of carrying out the hydrogenation and oxidation steps. However, they suffer the disadvantage of rapidly degrading to products which are incapable of being cyclically reduced and oxidized to product H_2O_2. Increasing the temperature at which the reduction or oxidation occurs further accelerates this side reaction, with the production of increased amounts of degradation products. Additionally, if the proportion of working compound which is hydrogenated per pass through the system (also termed "depth of hydrogenation") is increased, the amount of degradation rises sharply.

These conventional anthraquinone working compounds also undergo some nuclear attack during the catalytic hydrogenation step. This results in the gradual formation of tetrahydroanthraquinone derivatives. These compounds, unlike the degradation products reviewed above, will produce H_2O_2 upon cyclic reduction and oxidation. Moreover, the inclination to form unknown degradation products which cannot be reduced and oxidized to form H_2O_2 appears to be greater with the alkylated anthraquinones than with their tetrahydro derivatives.

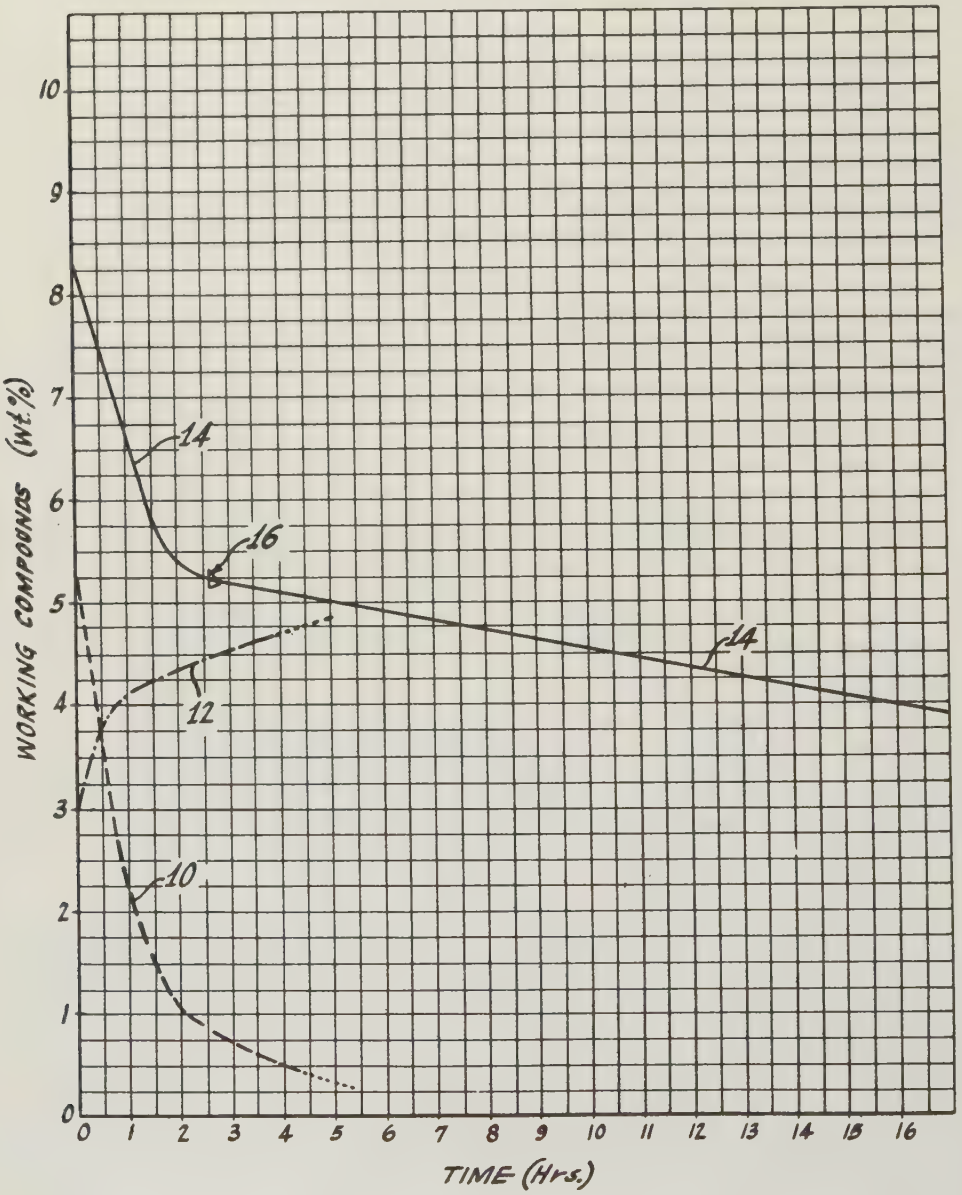
In spite of this, the art has not favored the conversion of the anthraquinone working compounds to their tetrahydro derivatives, or the use of these derivatives as working compounds, because of the difficulty encountered in commercially reducing and oxidizing tetrahydroanthraquinones to form hydrogen peroxide. This is clearly disclosed in U.S. Patent 2,739,042 issued to A.E. Corey et al, on March 20, 1956. In an effort to avoid working with the tetrahydro derivative, the patentees recite a method of regenerating anthraquinones from their corresponding tetrahydro derivatives. This is done by heating the tetrahydroanthraquinone-containing solution in the presence of a dehydrogenation catalyst to convert the tetrahydroanthraquinone to its precursor anthraquinone. This technique is designed to minimize the amount of tetrahydroanthraquinone formed in the cyclic process by including special processing steps for treating the work solution during cyclic operation.

Another procedure for reducing the formation of tetrahydro derivatives is taught in U.S. Patent 2,673,140. This is done by conducting the catalytic hydrogenation under very limited pressures, and by keeping the amount of hydrogenation (depth of hydrogenation) to very restricted amounts.

It has now been determined that a continuous process for producing hydrogen peroxide, by alternate reduction and oxidation of a tetrahydro derivative of an anthraquinone, can be carried out efficiently and economically, provided that the tetrahydro derivative is present in amounts greater than about 85% of the working compound; that it is hydrogenated to a depth of 55 to 80%; that it is contacted by air passed into the working solution through diffusers having pore diameters from about 0.006 to 0.015 inch at a flow rate of about 2 to about 4 cfm per square foot of oxidizing tower cross-sectional area, and for a minimum contact time of about 15 seconds.

In the present process the working solution contains the tetrahydro derivative of an anthraquinone in the amount of at least about 85% of the working compound or compounds present. This proportion of tetrahydro derivative is required in order to obtain the full benefit of its increased stability. This is illustrated by Figure 2.2 from data obtained in the example, subsequently to be described.

FIGURE 2.2: PLOTTING THE PROGRESS OF DEGRADATION OF THE WORKING SOLUTION AGAINST TIME, SHOWING THE AMOUNTS OF USABLE ANTHRAQUINONE CONTENT AT ANY MOMENT



Source: T.M. Jenney, D.H. Porter, U.S. Patent 3,073,680, January 15, 1963

In Figure 2.2, curve 10 represents the concentration of ethylanthraquinone (expressed as weight percent) in the work solution during the test. Curve 12 similarly represents the concentration of ethyltetrahydroanthraquinone in the work solution. As will be observed during the course of this test, curve 10 decreases in value, while curve 12 increases. This is due to the conversion of the ethylanthraquinone to ethyltetrahydroanthraquinone in the work solution, until virtually no ethylanthraquinone remains. Curve 14 represents the total amount of usable anthraquinones capable of producing hydrogen peroxide, including both the ethylanthraquinone and the ethyltetrahydroanthraquinone forms thereof, which are present in the work solution. In effect, curve 14 gives the additive numerical values of curves 12 and 10. The slope of curve 14 at any point illustrates the rate at which degradation of the working mixture proceeds, since it shows the amount of usable anthraquinone content at the start of the run and also the amount which remains at any point throughout the test period.

Point 16, on curve 14, is the point where the ratio of ethyltetrahydroanthraquinone to ethylanthraquinone reaches about 85% by weight of the total anthraquinone present. The sharp change in the slope of curve 14, at point 16, clearly shows the striking change in degradation rate of the working mixture, when it contains ethyltetrahydroanthraquinone in amounts over about 85% by weight.

Anthraquinones which may be converted to their tetrahydro derivatives and utilized in the process include 2-ethyl, 2-isopropyl, 2-sec-butyl, 2,5-butyl, 2-sec amyl, 1,3-dimethyl, 2-tertiary alcohol, the 2-methyl derivative, and others well known in the hydrogen peroxide art. The working solution containing the tetrahydro form of the working compound is subject to reduction in a hydrogenation zone in the presence of a catalyst. The catalyst employed is most suitably a noble metal catalyst, such as palladium deposited on an inert carrier. The carrier may comprise alumina, carbon, silica, silica alumina, calcium aluminum silicate, carbonates and others. Reduction of the tetrahydro derivative takes place in a "fixed bed" chamber.

In this type of catalytic hydrogenator, the catalyst is supported at the base of the hydrogenator on a perforated holder, and working solution is passed into the top of the hydrogenator concurrently with excess hydrogen. This mixture is reduced by mere contact with hydrogen in the presence of the catalyst, as it flows through the fixed bed. The proportion of working compound which is hydrogenated per pass (depth of hydrogenation) is at least about 55 to 80%. If higher depths of hydrogenation are desired, i.e., up to 90%, they may be carried out readily, but with some increase in the formation of degradation products. However, even if the instant process is operated to yield a 90% depth of hydrogenation, the buildup of degradation products is no greater than that obtained with conventional anthraquinones when operated to yield 50% depth of hydrogenation.

The working solution, after leaving the catalytic hydrogenator, is passed into an oxidizer. In the oxidizer, the working solution is oxidized by contacting the solution with air. In the normal mode of operation, the working solution flows continuously into the base of the oxidizing tank and is removed as oxidized overflow through a standpipe at the top of the oxidizing vessel. Air is pumped into diffusers located at the base of the oxidizing vessel and is released through the diffuser openings as a continuous upward flow of dispersed bubbles passing through the working solution.

The oxidation of the tetrahydroanthrahydroquinones is more difficult than corresponding hydroanthraquinones and requires specific operating conditions to carry out the oxidation on a commercial scale. The conditions under which oxidation takes place are critical, since the amount of oxidation which occurs is governed by the amount of oxygen mass transfer between the liquid phase (working solution) and the gaseous, or air phase. It has been found that the working solution should be passed through the oxidizer at rates not lower than about 400 to 600 liters per hour per foot^2 of tower cross-section in order to obtain maximum mass transfer. Flow rates below this amount result in substantially diminishing the mass transfer rate. Flow rates above this amount do not materially increase the rate of mass transfer per unit quantity of solution (mass transfer coefficient).

The rate of flow of air into the oxidizer also must be controlled carefully in order to obtain optimum oxidation of the working solution. The volume of air flowing through the oxidizer, which is generally at atmospheric pressure, although either subatmospheric or superatmospheric pressures may be employed, is maintained at between about 2 to about 4 cfm/ft.^{2}; that is, the volume of air passing through the column, regardless of the pressure within the tower, must measure between about 2 to about 4 cfm/ft.^{2} of oxidizing tower.

Contrary to what might be expected, supplying copious quantities of air into the oxidizer does not provide high mass transfer rates. When the flow of air into the oxidizing tower is maintained between 2 to 4 cfm/ft.^{2} of oxidizing tower, the mass transfer coefficient (oxidation rate) becomes desirably high. When flow rates of air above this range are employed, an unexpected sharp decrease occurs in both the mass transfer coefficient and in the volume of liquid contained in the oxidizing vessel. The sudden decrease in the liquid volume of the oxidizer, when a given air throughput is reached, is termed the liquid holdup breakpoint. Air flow rates above this point can never give high mass transfer rates because of the great decrease in volume of working solution present in the oxidizer.

When the rate of flow of air into the oxidizer is employed at below 2 cfm/ft.^{2} of oxidizing tower, the mass transfer coefficient again drops off quite considerably. As a result, oxidation of the working solution is incomplete and requires additional passes through the oxidizer to complete the oxidation. The size of the air bubbles which are released by the diffusers and which contact the working solution must also be subject to careful control. If extremely fine air bubbles, i.e., those obtained by employing diffusers having an average pore diameter below 0.005", are employed, small mass transfer coefficients are obtained. The finer air bubbles which are released by the smaller diameter diffusers appear to create an extremely stable foam in the oxidizing vessel. As a result, there is very little effective agitation and, consequently, a serious diminishing of mass transfer coefficient.

Additionally, the finer air bubbles cause the liquid holdup breakpoint in the oxidizing unit to be reached sooner; that is, the liquid holdup breakpoint is reached at a lower air flow than with coarser-sized air bubbles. Accordingly, the maximum air flow rate of finer air bubbles which can be passed through the oxidizer before reaching the liquid holdup breakpoint is low. This prevents greater volumes of air from effectively contacting the working solution. It has been found that diffusers having an average pore diameter of from 0.006 to 0.015" deliver air bubbles which give maximum mass transfer coefficients at air flows between 2 cfm to 4 cfm/ft.^{2} of oxidizing tower cross-section. An optimum pore diameter is between 0.008 to 0.011". If diffusers having an average pore diameter above these

values are employed, incomplete oxidation occurs and lowering of the mass transfer coefficient results.

In order to obtain sufficient duration of contact between the air phase and the working solution, or liquid phase, it has been determined that the height of a single-stage oxidizing tower should be at least about 100 inches tall. This height permits a contact time of at least about 15 seconds. Single-stage oxidation towers below this height do not allow sufficient time for the working solution and air phase to react completely. This results in erratic oxidation and inefficient oxidation, along with decreased hydrogen peroxide production. Multi-stage oxidation towers may be employed, provided that they permit the air phase to contact the working solution for a minimum total contact time of 15 seconds.

After the working solution is removed from the oxidizer, it is subjected to a water wash which dissolves the hydrogen peroxide in the aqueous phase. This aqueous phase containing the hydrogen peroxide is then separated from the residual working solution and sent to purifying units. The residual working solution is then recycled to the catalytic hydrogenator. The process, because of its extremely stable working compound, i.e., tetrahydroquinones, has many advantages. Among these is the ability to operate at higher temperatures without deleterious side effects. By increasing the temperature of operation, greater quantities of working compound can be dissolved in the working solution. As a consequence, more hydrogen peroxide is obtained per pass through the system.

Another advantage resides in the virtual elimination of quinone regeneration steps or, alternatively, in steps for removal of degraded by-products. The tetrahydro derivatives employed as the working compounds have such increased stability compared to their precursor anthraquinones that the amount of degraded by-products is materially reduced. As a result, additional process steps are not required for removing these by-products.

Another advantage resides in the high concentration of peroxide which is formed in the working solution. This may be attributed either to the increased temperatures of operation or to the increased depth of hydrogenation of the working solution. That is, more working compound is alternately reduced and oxidized per pass through the system due to an increased depth of hydrogenation, or alternately by dissolving more working compound in the working solution at the higher operating temperatures. The increased quantity of working compound passed through the system produces more hydrogen peroxide per unit of working solution. This results in an increase in peroxide concentration in the work solution. Upon aqueous extraction of the work solution, the increased amounts of peroxide are absorbed in the aqueous phase resulting in an aqueous extract having a higher concentration of peroxide.

Increased peroxide concentration in the aqueous extract is extremely desirable. It is advantageous because higher concentrations of peroxide in the aqueous phase permit more efficient extraction. Furthermore, it reduces the amount of distillation required to purify the hydrogen peroxide product. As a result, the distillation step can be simplified and the time required for distillation can be reduced. The following example is given to illustrate the process.

A run was made under total recycle conditions in the hydrogenator as described below in order to compare the degradation rate of 2-ethylanthraquinone and 2-ethyltetrahydro

anthraquinone. This recycle test accelerates reaction conditions in the hydrogenator, and can be used to determine rapidly the rate at which working compounds will be converted into unusable anthraquinone derivatives by the catalyst.

A fixed bed hydrogenator was charged with a catalyst comprising 1.0% palladium on an activated alumina carrier, and having a particle size of 10 to 20 mesh. A total of 2.5 liters of a work solution comprising 61 weight percent dimethylnaphthalene as the quinone solvent and 39 weight percent trioctylphosphate as the hydroquinone solvent was passed downwardly through the hydrogenator with excess hydrogen at a pressure of 35 psia and at a temperature of 50°C. The original solution contained an anthraquinone composition indicated in the following chart. The working solution which passed through the hydrogenator was recycled to the top of the hydrogenator along with more hydrogen, in a continuous cycle. Periodic analyses of the working solution were made to determine the usable anthraquinone composition, and these results are reported below.

Time (Hrs.)	Useable Anthraquinone Composition (Wt. Percent)		
	Total	2-Ethyl Anthraquinone	2-Ethyl Tetrahydro-Anthraquinone
0	8.4	5.4	3.0
0.25	8.0	4.8	3.2
0.50	7.7	4.0	3.7
1	6.3	2.2	4.1
2	5.3	1.0	4.3
4	5.2	0.5	4.7
7	4.7		4.7
11	4.4		4.4
15	4.2		4.2
17	3.9		3.9

Anthraquinone Carboxylic Esters Have Excellent Solubility in All Solvents and therefore Enable High Yields

FMC; Käbisch, G. and Läufer, S. (4): It has been found that esters of monobasic or dibasic anthraquinone carboxylic acids, or their tetrahydro derivatives, are excellent working compounds. The alcoholic component of these esters can be aliphatic or cycloaliphatic. If aliphatic, they can be monohydric or polyhydric; they can be straight-chain or branched, and can contain other groups, e.g., aromatic or alkoxy substituents on the aliphatic chain.

The present anthraquinone carboxylic esters have many advantages over the more conventionally employed anthraquinone working compounds. Among them is the excellent solubility of these esters with all conventional solvents which have been suggested for use in the anthraquinone process, so that they are not restricted to a specific solvent. Additionally, the tetrahydroanthraquinone carboxylic esters which result from nuclear hydrogenation of their corresponding precursor esters show this increased solubility not only in the quinone form but also in the reduced form of the ester. Since these tetra compounds can be reduced and oxidized cyclically to produce hydrogen peroxide, any gradual conversion of the anthraquinone carboxylic ester to its corresponding tetrahydro derivative does not remove the advantageous solubility possessed by the nonnuclear hydrogenated anthraquinone esters.

It has been determined further that the excellent solubility of these anthraquinone carboxylic esters may be increased even more if the alcohol component, which is used for esterifying the carboxylic acid, is at the same time also a component of the solvent, or at least possesses a similar structure to the alcohol component. Thus, while the present class of working compounds can be used with any universally employed solvent with increased solubility, even greater solubilities can be obtained if one employs the alcohol component as one of the working solvents. The present class of working compounds, because of their increased solubility in working solvents, permits the anthraquinone process to be carried out in an open-air plant without the problem of crystallizing out some of the working compound dissolved in the solvent. Therefore, the insulation or mild heating, which must be applied to both containers and pipe lines carrying working solutions containing conventional working compounds, need not be resorted to when employing these working compounds.

Another advantage which the present anthraquinone carboxylic esters have over the more conventional working compound, such as 2-ethylanthraquinone, is a greater increase in the solubility of the hydroquinone form of this working compound. In the past it was found that the hydrogenated form of the working compound was always more difficult to dissolve than the oxidized form. As a result, special solvent mixtures had to be employed in order to dissolve the hydrogenated form of the anthraquinone being employed. This in turn reduced the amount of quinone solvent available for dissolving the oxidized form of the anthraquinone, and further decreased the amount of working compound which could be dissolved in the working solution. The increased solubility of the present working compound, in both the quinone form and hydroquinone form, permits the proportion of solvent used to dissolve the hydrogenated anthraquinone in the working solvent to be reduced markedly. Thus, increased amounts of both oxidized and reduced working compound are circulated per pass through the process.

Still another advantage of the present anthraquinone carboxylic esters is their relatively inexpensive and ready availability on a commercial scale. These esters can be obtained in over 90% yields from readily available anthraquinone carboxylic acids by merely esterifying them with the desired monohydric or polyhydric alcohols. The specific esters which are the preferred embodiments of the present process are those of anthraquinone monocarboxylic acid and anthraquinone dicarboxylic acid which have low melting points. These low melting point esters have been found to have a preferred high solubility in conventional solvents for the anthraquinone process. This correlation permits selection of those esters that have high solubility by determining their melting points.

The first group of these low-melting anthraquinone monocarboxylic esters are those produced from primary monohydric alcohols. The aliphatic chain of these alcohols can be either straight or branched and preferably should contain between about 5 to 11 carbon atoms. It is further understood that the aliphatic chain of these alcohols may contain other substituents such as alkoxy, aromatic, or cycloaliphatic groups. The following example illustrates the method for producing these esters and the desirable results obtained when utilizing these esters.

A mixture of 12.6 g. of 2-anthraquinone carboxylic acid (M.P. 294°C.) and 11.6 g. of n-heptanol (M.P. 176°C.) was added to toluene as the reaction medium. To this mixture was added 0.5 g. of p-toluene sulfonic acid as the catalyzing agent. The mixture was

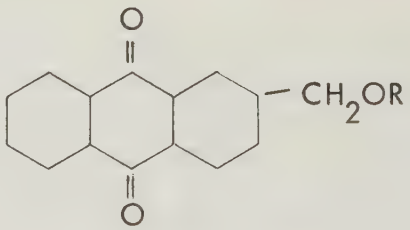
refluxed for 17 hours, during which the resulting reaction water was continuously drawn off. The major amount of excess heptanol was then distilled off. The reaction product was twice purified by chromatography using Brockmann Al_2O_3 in a column, and a total of 16.5 g. (94.3% of theory) was recovered. It had a melting point between 68° to 71.5°C., and after recrystallization from gasoline had a melting point of 72° to 73°C. This component was identified as 2-anthraquinone carboxylic n-heptyl ester.

In a similar manner, other esters of 2-anthraquinone carboxylic acid were prepared using primary, unbranched alcohols having varying carbon chains. The esters so prepared and their melting points are tabulated below.

Alcoholic component of ester	Carbon atoms	Melting point ° C.
Methyl	1	167
Ethyl	2	147
n-Propyl	3	116
n-Butyl	4	123
n-Amyl	5	92
n-Hexyl	6	89
n-Heptyl	7	77
n-Octyl	8	87
n-Nonyl	9	92
n-Decyl	10	94
n-Undecyl	11	92
n-Dodecyl	12	97

Ethers of 2-Hydroxymethylanthraquinone and a Non-Tertiary Alcohol Are Highly Soluble in Organic Solvents, both in the Reduced and Oxidized Forms

Air Liquide; Etienne, A. and Izoret, G. (5): A new series of compounds are proposed as working materials in H_2O_2 manufacture, viz. the ethers of 2-hydroxymethylanthraquinone and a non-tertiary (primary or secondary) alcohol, and their manufacture is described from 2-chloromethylanthraquinone, which compound is readily obtained directly from 2-methylanthraquinone. The ethers may be represented by the general formula:



where R is a residue of a non-tertiary alcohol and is a member selected from the group consisting of saturated alkyl, haloalkyl, hydroxyalkyl, alkoxyalkyl, dihydroxyalkyl, dialkoxyalkyl, arylalkyl and cycloalkyl radicals.

The yield of peroxide with the above ethers was ascertained as follows. A solution of one millimole ether in the chosen solvent, which should theoretically give one millimole hydrogen peroxide, was hydrogenated in the presence of 100 mg. catalyst (0.6% palladium on alumina) until the hydroquinone was formed (which corresponds to the adsorption of one millimol hydrogen, i.e., about 24 cc. at 20°C.). The catalyst was then separated through

filtration in an atmosphere of hydrogen, and the solution of hydroquinone was reoxidized through air bubbling. The hydrogen peroxide was extracted from the solution through washing with three 10 cc. portions of distilled water, then determined with a 0.1 N potassium permanganate solution. The organic solution of the quinone form of the ether was then evaporated to dryness, and its identity with the initial product established. For all the ethers, the yield of hydrogen peroxide was between 90% and 100%.

Anthraquinone Disulfonic Acid Salts as Working Materials Enable Utilization of Cheap By-Product Hydrogen Sulfide for the Reduction Stage

Canadian Industries Ltd.; Lusby, G.R. (6): This worker proposes a novel variation of the anthraquinone process by using as working material anthraquinone disulfonic acid salt and effecting its reduction with H_2S.

Hydrogen sulfide is produced extensively as a by-product from natural gas and petroleum, and it is known to produce sulfur therefrom by oxidation. It has now been found that hydrogen sulfide can be used as a raw material in the production of hydrogen peroxide. Broadly speaking, the process comprises reacting an hydrogen sulfide gas with an alkaline aqueous solution of a salt of an anthraquinone disulfonic acid, thus producing elemental sulfur and the reduced anthraquinone disulfonic acid salt; separating the sulfur; and oxidizing the reduced salt to form hydrogen peroxide, thereby regenerating the starting anthraquinone disulfonic acid salt.

The hydrogen sulfide gas suitable for the process may be pure hydrogen sulfide, or it may be a gas containing hydrogen sulfide and a gaseous hydrocarbon. However, the presence of oxygen in the hydrogen sulfide-containing gas will decrease the yield of hydrogen peroxide. The anthraquinone disulfonates suitable as reactants in this process include the sodium salts of the known isomers of anthraquinone disulfonic acid and mixtures thereof. The disodium salt of anthraquinone 2,7-disulfonic acid is the most water-soluble of the isomeric sodium salts and, being commercially available, is the preferred reagent. However, the less soluble salts of the other isomers of anthraquinone disulfonic acid can be used at lower concentrations, but the yield of hydrogen peroxide will be less than when the 2,7-disulfonic acid derivative is employed.

In the preferred embodiment of the process, an aqueous solution containing from 10 to 150 grams per liter of disodium anthraquinone 2,7-disulfonate, about 10 grams per liter of boric acid and sufficient sodium hydroxide to bring the solution to a pH about 9 is employed. The hydrogen sulfide gas is introduced into this solution by a dispersing device and the reacting mixture is agitated, the reaction producing elemental sulfur and the reduced anthraquinone disulfonate. The excess hydrogen sulfide is removed by passing carbon dioxide through the reaction mixture and the sulfur is separated from the reduced anthraquinone derivative by filtration. The reduced anthraquinone derivative is then regenerated by aerating the solution after the addition of lime.

It has been found that better yields of hydrogen peroxide are obtained when lime is added to the reduced solution at the beginning of the oxidation stage. The precipitate of calcium peroxide is separated by filtration and the hydrogen peroxide recovered by the known decomposition of calcium peroxide with carbon dioxide. The regenerated disodium

anthraquinone 2,7-disulfonate can then be again reduced with hydrogen sulfide and the cycle repeated.

In addition to producing hydrogen peroxide, the process can be modified to produce oxygen. Instead of isolating the hydrogen peroxide formed by the oxidation of the reduced anthraquinone derivative, the solution containing the hydrogen peroxide is passed over a hydrogen peroxide decomposition catalyst such as ferric oxide, manganese dioxide, silver or copper. The oxygen liberated is then separated from the aqueous solution and dried. The process is more fully illustrated by the following example.

3.5 liters of a solution containing 100 grams per liter of disodium anthraquinone 2,7-disulfonate, 10 grams per liter of boric acid, and sufficient sodium hydroxide to give a pH of about 9, was stirred by a single blade impeller, the temperature being maintained at 25°C. A stream of 100% hydrogen sulfide gas was passed into this solution through a gas disperser located below the stirrer. Precipitation of sulfur commenced about 7 to 8 minutes after the start of the introduction of hydrogen sulfide. At the end of 3 1/2 hours, the flow of hydrogen sulfide was stopped and carbon dioxide gas was passed through the solution for 2 hours to remove excess hydrogen sulfide.

The resulting mixture was filtered and 19.5 grams of crystalline sulfur were collected, corresponding to a 71.8% yield, based on the quinone content of the solution. 69 grams of calcium hydroxide representing about a 10% excess over that required for a stoichiometric yield of hydrogen peroxide were added to the filtrate which was then aerated. The precipitate was filtered off and analyzed for available oxygen. A precipitate containing 19.7 grams of calcium peroxide was recovered. This corresponded to a 32.2% yield of hydrogen peroxide based on the quinone content of the solution and a 45% yield based on the sulfur produced. The remainder of the solid precipitate consisted mainly of slime and some calcium carbonate. The calcium peroxide precipitate produced was slimy in nature and very slow to filter. During the operation the evolution of gas, believed to be oxygen, from the slurry was observed.

Separation of Disodium Salt of Anthraquinone Disulfonic Acid from Calcium Peroxide Precipitate

Canadian Industries Ltd.; Hoey, G.R., and Hudson, D. (7): In Canadian Patent 673,355 issued on October 29, 1963, a process is disclosed for the manufacture of hydrogen peroxide by the reduction of the disodium salt of anthraquinone disulfonic acid with hydrogen sulfide and subsequent oxidation of the reduced product with oxygen. [See also the previous process (6).] The resulting hydrogen peroxide is separated from the alkaline disodium anthraquinone disulfonate solution by precipitation as calcium peroxide by the addition of calcium hydroxide at room temperature. In carrying out this process, it has been found difficult to completely separate the anthraquinone disulfonic acid salt from the precipitated calcium peroxide. The calcium peroxide product is fine grained and usually contains several percent of anthraquinone disulfonic acid salt. This cannot be removed even by the use of uneconomically large amounts of wash water. Since the process recycles the anthraquinone disulfonic acid salt solution, economic operation requires that an efficient separation of the latter be employed. In addition, the adsorbed anthraquinone disulfonic acid salt contaminates the hydrogen peroxide product.

It has now been found that effective separation of the anthraquinone disulfonic acid salt solution from the calcium peroxide precipitate can be attained if the calcium peroxide is precipitated in the form of coarse crystals of calcium peroxide octahydrate.

A desirable aid to the obtaining of anthraquinone disulfonic acid sodium salt-free crystals of calcium peroxide octahydrate is a stable hydrogen peroxide containing solution. The cationic impurities can conveniently be removed by ion exchange resins. It has also been found that calcium peroxide octahydrate changes to the dihydrate form at temperatures above 40°C. However, the temperature of transition is lowered by the presence of hydrogen peroxide in the surrounding aqueous solution. At 20°C. the octahydrate form is not stable for long periods in concentrations of hydrogen peroxide greater than 0.25% and at 25°C. the maximum concentration of hydrogen peroxide for long term stability of the octahydrate is 0.009%. However, the octahydrate form of calcium peroxide appears to be capable of existence in a metastable form for short periods of time at higher concentrations of hydrogen peroxide than indicated hereinbefore.

The presence of seed crystals of calcium peroxide octahydrate in the hydrogen peroxide containing anthraquinone disulfonic acid sodium salt solution aids in the forming of suitable precipitates. These seed crystals may be added to the solutions or may be present through a continuous process of precipitation.

It has been found that the preferred procedure for precipitating calcium peroxide is to run the aqueous solution of reduced anthraquinone disulfonic acid salt slowly into a well stirred precipitator containing a continuously aerated solution or slurry of calcium hydroxide in excess of the amount required to precipitate the calcium peroxide. The ingredients are maintained below 30°C. The calcium hydroxide concentration is maintained by the continuous addition of calcium hydroxide. In this procedure the hydrogen peroxide concentration in the precipitator will remain at a value less than the stoichiometric equivalent of the calcium hydroxide present. The calcium peroxide octahydrate precipitate prepared in this manner is readily washed free of anthraquinone disulfonic acid sodium salt. In addition, the residual hydrogen sulfide in the solution will not reduce the yield of calcium peroxide octahydrate.

The use of a solution of calcium hydroxide gives calcium peroxide octahydrate precipitates containing less adsorbed anthraquinone disulfonic acid sodium salt than the use of calcium hydroxide slurries. It has been observed that when an aqueous solution of calcium hydroxide is added to an aqueous 0.6% solution of hydrogen peroxide containing dissolved anthraquinone sulfonic acid sodium salt, it is possible to obtain a precipitate at room temperature of calcium peroxide octahydrate in spite of the high concentration of hydrogen peroxide. It is believed that the octahydrate crystals so formed are metastable.

When solid calcium hydroxide is added directly to an aqueous solution of hydrogen peroxide containing anthraquinone disulfonic acid sodium salt, the precipitate formed is fine grained and the adsorbed anthraquinone disulfonate cannot be washed free from the crystals with water. The precipitated calcium octahydrate can be conveniently separated from the anthraquinone disulfonic acid salt-containing mother liquor by centrifuging and washing the residual mother liquor from the solid with water. The solid calcium peroxide can then be dried by known procedures.

Alternatively, the calcium peroxide octahydrate after separation from the mother liquor may be converted to solid anhydrous calcium peroxide by immersion in a dilute aqueous solution of hydrogen peroxide at about 30°C. Washing of the anhydrous calcium peroxide product with acetone at room temperature provides a material containing only trace amounts of the anthraquinone disulfonic acid salt.

The calcium peroxide produced by this process may be employed as such or may be used for the production of hydrogen peroxide or of oxygen by known methods. When the calcium peroxide is converted to hydrogen peroxide, it is essential to remove trace impurities before the hydrogen peroxide is concentrated by distillation. Metallic impurities may be removed by passage of the aqueous hydrogen peroxide solution through a cation-exchange resin such as the sodium salt of the well known sulfonated styrene-divinylbenzene copolymers. Traces of anthraquinone disulfonate remaining in the aqueous hydrogen peroxide solution can be removed by passage through a bed of activated carbon prior to distillation. Removal of the traces of anthraquinone disulfonates in this manner may permit simplification of the distillation process in that the solution need only be concentrated by evaporation of water without the necessity of distilling off the hydrogen peroxide.

The process is more fully illustrated by the following examples. A series of solutions was prepared containing 0.5% by weight of hydrogen peroxide and varying amounts of anthraquinone, 2,7-disulfonic acid disodium salt (ADA) dissolved in water. The hydrogen peroxide was precipitated as calcium peroxide octahydrate by the addition of a soluble calcium compound. In some cases seed crystals of calcium peroxide octahydrate were present.

TABLE 2.1: RESULTS OF SEPARATIONS

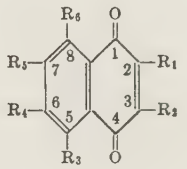
Ex.	Calcium source	Concentration of ADA in solution, percent	Seed crystals, percent of product	pH during precipitation	Weight [1] of wet cake, grams	Solid	Volume of wash water, millilitres	Total inorganic solids in precipitate, percent	ADA in product, percent of total inorganic solids	Percent Calcium peroxide in form of $CaO_2.8H_2O$
1	Solid reagent $Ca(OH)_2$.	12.2	0		260	Unwashed cake	0	34.2	23.7	
						Washed cake	534		16.1	30.0
						do	1,500		8.8	
2	do	8.1	0		260	Unwashed cake	0	32.9	17.6	
						Washed cake	1,632	33.4	5.6	
						After reslurrying with H_2O.	2,755	34.2	4.4	78.0
						Partially dehydrated	3,375	49.3	4.35	
3	do	0.5	0		260	Unwashed cake	0	37.1	13.3	
						Washed cake	1,869	37.7	6.4	
						After reslurrying with H_2O.	3,097	36.8	7.4	38.0
						Partially dehydrated	3,495	59.1	7.2	
4	Calcium chloride.	5.2	0	11-12	273	Unwashed cake	0	30.1	4.26	
						Washed cake	1,112	30.5	2.73	96.5
5	do	5.1	33	10-11	110	Unwashed cake	0	18.4	0.99	
						Washed cake	650	23.8	0.03	
6	do	8.9	50		163	Unwashed cake	0	32.0	2.1	
						Washed cake	468	31.0	0.39	99.0
7	Solid reagent $Ca(OH)_2$.	4.6	50		115	Unwashed cake	0	26.9	5.5	
						Washed cake	477	27.3	1.4	100
8	Dissolved reagent $Ca(OH)_2$.	1.7	0		[2] 3	Washed cake	30	30.0	2.23	
9	do	9.5	25		[2] 10	do	100	30.5	1.12	
10	do	9.5	15	10.6	162	Unwashed cake	0	30.1	2.89	
						Washed cake	456	28.8	0.52	100
11	do	11.0	30	10.6	154	Unwashed cake	0	31.4	1.63	
						Washed cake	352	31.1	0.02	100
12	Dissolved commercial $Ca(OH)_2$.	11.0	30	10.6	160	Unwashed cake	0	29.5	2.76	
						Washed cake	351	30.5	0.08	100

[1] Unless otherwise stated the precipitates were centrifuged.
[2] Filter.

Sodium chloride was added to the solution to act as a tracer to determine the amount of free water in the precipitates. The calcium peroxide was precipitated at a temperature of 1° to 3°C., separated by centrifuging and the precipitate washed with water. The results of the separations are shown in Table 2.1. The percentages are by weight. The effectiveness of employing seed crystals of $CaO_2 \cdot 8H_2O$ in reducing the anthraquinone disulfonic acid salt retained on the washed precipitate is clearly shown.

Alkyl Naphthoquinones Have Improved Solubility and Stability towards Over-Reduction and Oxidative Degradation

Laporte Chemicals Ltd.; Logan, W.R., and Braid, J.E. (8): In this process the working solution contains at least one naphthoquinone having the general formula:



in which R_1 and R_2, which may be the same or different, represent alkyl groups having up to 9 carbon atoms, and R_3 to R_6, which may be the same or different, represent hydrogen atoms or alkyl groups having up to 9 carbon atoms. Conveniently the alkyl groups contain up to 6 carbon atoms; those with 1 to 4 carbon atoms being especially suitable.

Normally it is preferred that the solute consist of one or more of the naphthoquinones; that is to say, the naphthoquinones will not normally be employed in association with other known compounds, for example, alkyl anthraquinones. If a 2,3-alkyl disubstituted naphthoquinone is to be employed (i.e., R_1=R_2=alkyl up to C_9; R_3 to R_6=H), the 2,3 diethyl, 2-methyl-3-ethyl, 2-methyl-3-n-butyl, and (especially) 2-methyl-3-n-propyl compounds are suitable. One suitable trisubstituted compound is 2,6-dimethyl-3-ethyl naphthoquinone (R_1=R_4=methyl; R_2=ethyl; R_3=R_5=R_6=H).

One method of preparation of 2-methyl-3-ethylnaphthoquinone is described in J.C.S. 1953, 1196; the starting material being 2-methylnaphthoquinone, which can be obtained by oxidizing 2-methylnaphthalene. By starting with 2-ethylnaphthalene and following the same procedure 2,3-diethyl naphthoquinone is obtained. By starting with 2,6-dimethyl naphthalene then 2,6-dimethyl, 3-ethylnaphthoquinone can be obtained. The preparation of the 2-methyl-3-n-propyl and 2-methyl-3-n-butyl naphthoquinones is conveniently effected by starting with 2-methyl naphthalene. This is first oxidized to the corresponding naphthaquinone in known manner and is then alkylated by the tetravalent-lead ester alkylation method described in J.A.C.S. 1942, 64, 2043.

Suitable solvents for the working solution include, for example, (a) mixtures of benzene or polyalkyl benzenes with esters of cyclohexanol and/or alkylcyclohexanols, e.g., 50/50 v./v. of benzene and methyl cyclohexanol acetate (sextate), and (b) hydrocarbon/ketone mixtures, the ketone being, for example, diisobutyl ketone.

Several advantages accrue from the process. For instance, the stability of substituted naphthoquinones having the above formula towards over-reduction is most marked. It has been found that the rate of hydrogen uptake of the fully reduced form of the diethyl compound is only 1/567 of the rate of hydrogen uptake during the conversion of quinone to quinol. Again, the stability of the quinone form towards oxidative degradation is good. In addition to this good stability, the disubstituted and higher substituted naphthoquinones having the above general formula possess improved solubility in the working solution and, consequently, greater capacity for producing hydrogen peroxide.

Naphthoquinones which contain no, or only one, alkyl substituent in the quinonoid ring are not suitable for use as hydrogen carriers, since they produce quinols which do not undergo sufficiently rapid autoxidation. Also, they are more susceptible to oxidative degradation by hydrogen peroxide and oxygen than the 2,3-disubstituted quinones. The same disadvantages are possessed by disubstituted naphthoquinones having one substituent in each ring. The following example further illustrates the process, showing autoxidation rates.

2,3-diethyl-naphthoquinone dissolved in a 50/50 v./v. mixture of organic solvents, to the extent of 10 g./liter of solvent, was reduced to the quinol in 6 minutes at 25°C. with hydrogen at atmospheric pressure in the presence of a catalyst comprising 2% palladium on an inert support. The fully reduced solution, after removal of catalyst, was oxidized with oxygen in 9.5 minutes under the same conditions of temperature and pressure. The hydrogen peroxide produced was extracted with water in 99.5% yield.

WORKING SOLVENTS AND SOLVENT MIXTURES

Many solvents have been suggested for use in the manufacture of hydrogen peroxide by the anthraquinone process. However, because of the large number of requirements for a suitable solvent in this process, most of these have been found unsuitable. In order that a solvent be satisfactory in this operation, it should have as many as possible of the following ideal properties:

(1) It must dissolve a large amount of the anthraquinone.
(2) It must dissolve a large amount of the anthrahydroquinone.
(3) It must be chemically inert, particularly to oxidation and hydrogenation.
(4) It must be a low-cost, commercial product, free of contact poisons.
(5) It must have a high boiling point and a high flash point.
(6) It must have a low degree of solubility in water.
(7) Its distribution coefficient for hydrogen peroxide must be high.

This list of important properties could be enlarged. Because of these stringent requirements, mixtures of solvents are commonly used, in an endeavor to approximate the desired properties of an ideal solvent by a suitable combination of the individual constituents.

Generally, the patents which cover this field stress the use of solvent mixtures, one component of which is a specific solvent for the quinonic form, while the other a specific solvent for the hydroquinonic form. The components are contained in the mixture in variable proportions, depending upon the solvent power required for each of the two forms.

These mixtures usually contain a higher proportion of the specific solvent for the hydroquinonic form than of the solvent for the quinonic form, since the hydroquinonic form generally has a markedly lower solubility. This necessarily results in a substantial limitation of the amount of hydrogen peroxide obtainable. The highest proportion of hydroquinonic form which can be kept in solution by the given amount of specific solvent governs the amount of hydrogen peroxide obtainable.

More specifically, U.K. Patent 465,070 gives as examples of suitable solvents for the anthraquinols, amyl alcohol, cyclohexanol and methyl-cyclohexanol, while the solvent specified for the anthraquinone is benzene, toluene, xylene or tetrahydronaphthalene. Various other solvents have subsequently been proposed for use in such a process. Thus, in U.K. Patent 508,081 the solvent specified in the example is a mixture of benzene and methyl-cyclohexanol. U.K. Patent 669,274 describes the use of a solvent mixture consisting of a hydrocarbon constituent for solution of the quinone material and a water-insoluble organic phosphonate for dissolving the anthraquinol. Examples of hydrocarbons given are benzene and dimethylnaphthalene. U.K. Patent 671,254 describes a solvent mixture with the usual hydrocarbon constituent for the quinone form, while the solvent for the quinol form of the alkylated anthraquinone is a trisubstituted organic ester of phosphoric acid. Examples of hydrocarbons given are benzene and dimethylnaphthalene.

In U.S. Patent 2,215,883 suitable solvent mixtures are, for example, benzene and cyclohexanol, toluene and amyl alcohol, xylene or anisol and isoheptyl alcohol and anisol and methyl-cyclohexanol. U.S. Patent 2,455,238, however, describes a single solvent having the requisite solvent power for the quinone as well as the quinol form and in which both reduction and oxidation can be carried out at relatively high concentrations of both forms of the working intermediate. Examples of such single solvents are esters of sebacic acid or the esters of other dibasic organic acids, such as succinic and adipic acid, the molecular structure of the ester containing twelve to sixteen carbon atoms, containing two ester groups and being made from an aliphatic or aryl-aliphatic acid and an aliphatic or aryl-aliphatic alcohol. The patent mentions a number of esters including di-p-methyl-cyclohexyl succinate.

U.K. Patent 686,567 describes a solvent mixture consisting of the primary and secondary nonyl alcohols, and mixtures thereof, and a substance selected from the group consisting of the monomethyl and dimethyl substituted naphthalenes and mixtures thereof.

The component for dissolving the anthraquinhydrone or anthraquinol can also influence the ease of aqueous extraction of the hydrogen peroxide produced when the other component in the solvent mixture is an aromatic hydrocarbon, e.g., benzene, as the partition coefficient of hydrogen peroxide between the water and the solvent mixture depends largely upon it. The solvents previously proposed, and illustrated above, for dissolving the anthraquinhydrone or anthraquinol had, however, several disadvantages. Thus, cyclohexanol is a good solvent for the anthraquinhydrone or anthraquinol, but it is very soluble in water and is oxidized to adipic acid by hydrogen peroxide. Both amyl alcohol and methyl-cyclohexanol have an inconveniently high solubility in water. The partition coefficients also of the mixtures of cyclohexanol, methyl cyclohexanol and amyl alcohol with the solvent for the anthraquinones are low.

On the following pages, in this section, a number of novel solvents and solvent systems

are put forward for use in the anthraquinone process, which are claimed to possess several advantages over previously used materials.

Methyl Cyclohexanol Acetate

Laporte Chemicals Ltd.; Le Feuvre, C.W. (9): The process is based upon the discovery that the acetates and propionates of cyclohexanol and of alkyl cyclohexanols, particularly methyl cyclohexanol and preferably methyl cyclohexanol acetates are excellent solvents for the process, either when used alone or as components of solvent mixtures. Preferably the alkyl group or groups in the alkyl cyclohexanols do not contain more than eight carbon atoms. The term "alkyl cyclohexanol" as used here includes not only the separate isomers, but also a mixture of any or all of the isomers.

The use of a single solvent as distinct from a solvent mixture has a number of advantages as follows:

(1) It is simpler to use a single solvent than a mixture of solvents. It obviates the trouble of maintaining the proportion of the two solvents in a solvent mixture.
(2) It obviates the use of benzene and similar solvents with a low flash point, as the cyclohexanol esters have a higher flash point.
(3) Owing to the higher solubility of the quinol form in a single solvent, a greater quinol concentration can be used, and hence there is less solution to handle than when using a solvent mixture, for the same hydrogen peroxide output.

Examples of esters suitable for use in the process are the acetic acid or propionic acid esters of cyclohexanol or of methyl cyclohexanol (in this latter case the 1, 2, or 3 isomers or a mixture of them). If a solvent mixture is used, the solvent for the quinone may be benzene. Benzene, usually employed as the solvent for the quinone has, however, the serious disadvantage of having a low flash point and high vapor pressure. In addition benzene vapor is highly toxic so that not only are there fire risks, but also possible health hazards for the plant operators. In a process in which gases are blown through a mixture containing benzene and then to waste, its low vapor pressure necessitates an expensive solvent recovery process. It is therefore proposed to employ as the solvent for the quinone one or more benzenes containing one or more alkyl groups, e.g., ethyl or methyl substituted benzenes.

In addition to having a higher flash point, the benzenes containing one or more alkyl groups, e.g., ethyl or methyl substituted benzenes, also have other advantages. With increasing substitution, the vapor pressure and toxicity decrease. Thus, by a suitable choice of solvent, fire and other hazards can be greatly decreased, while the necessity for solvent recovery processes can be largely eliminated. Another advantage is that the control of solvent proportions is simplified as this can be difficult when one of the components of the solvent mixture is more volatile than the other, which is generally true with benzene.

The alkyl substituted benzenes may be, for example, one or more xylenes or one or more trimethyl-benzenes. An example of a suitable methyl substituted benzene is a proprietary solvent derived from petroleum and having a boiling range of 5% at 155°C. and 95% at 185°C. The proportion of aromatic compounds to paraffinic in this solvent is of the order 4:1. It contains 50% of mesitylene (1,3,5-trimethylbenzene), 30% of pseudocumene

(1,2,4-trimethylbenzene) and 1,3,4-trimethylbenzene. The remaining 20% are paraffinic compounds. The above solvent has a flash point of 105°F. and a specific gravity of 0.855; another similar solvent has a flash point of 125°F. and a specific gravity of 0.870. Another example is a mixture of xylene isomers, obtained from a petroleum source, which has a specific gravity of about 0.855, with a flash point of 75°F. Furthermore, other commercial alkyl substituted benzenes may be used and, if desired, may be purified by conventional methods before use in the process.

The use of an acetate or propionate of cyclohexanol or of an alkyl cyclohexanol results in a number of advantages as compared with the customary solvents such as cyclohexanol and amyl alcohol. Thus, the acetates and propionates of cyclohexanol and alkyl cyclohexanols have a lower water solubility and they are more resistant to oxidation. Although the solubility of the anthraquinhydrone or anthraquinol in them is less than in the corresponding cyclohexanol, the hydrogen peroxide is more easily extracted as they have a higher partition coefficient. Furthermore, the acetates and propionates of cyclohexanol and of alkyl cyclohexanols have advantages over the solvents of U.S. Patent 2,455,238, as is shown by the following experiments comparing the dimethyl cyclohexanol succinate and methyl cyclohexanol acetate.

A solution of 60 g. of 2-ethylanthraquinone in one liter of methyl cyclohexanol acetate was made, and its density at 20°C. was found to be 0.959 g./cc. A solution of 60 g. of 2-ethylanthraquinone in one liter of dimethyl cyclohexanol succinate was made, and its density at 20°C. was found to be 1.038 g./cc. These results showed that the dimethyl cyclohexanol succinate would be unsuitable as a single solvent because the density of the solution would make it inconvenient for water extraction of the hydrogen peroxide. The viscosity of the solvent or solvent mixture is of considerable importance because a high viscosity leads to a slower rate of hydrogenation, slower filtration, greater difficulty in pumping, etc. The viscosity of methyl cyclohexanol acetate is 2.19 centipoises at 20°C., while the viscosity of dimethyl cyclohexanol succinate is 70.1 centipoises at 20°C.

Comparative experiments were carried out in which, for the solvent mixture, a solution was taken containing 90 g./liter of 2-ethylanthraquinone in a 50:50 xylene-ester solution and hydrogenated using 1 g. of 2% palladium on alumina catalyst in 100 cc. of the solution. The hydrogen uptake in the case in which the ester was methyl cyclohexanol acetate was 27 cc. of hydrogen per minute, while in the case in which the ester was dimethyl cyclohexanol succinate, it was 11 cc. of hydrogen per minute.

The solubility of the reduced form of the quinone in solvent mixtures, each containing one of the two esters, is also of importance. Determinations of these were made in the following way: The solubility of the 2-ethylanthraquinhydrone was determined by hydrogenating a solution of the quinone in the solvent mixture with a suitable hydrogenation catalyst until precipitation of the quinhydrone occurred. The solution was then filtered and shaken with oxygen until the dissolved quinhydrone was oxidized. The concentration of hydrogen peroxide in the oxidized solution was determined; this was equivalent to the quinhydrone concentration, or to the quinhydrone solubility. The results were obtained using a 50:50 xylene-ester solvent mixture at 20°C. and the results for the quinhydrone solubility expressed as equivalent g./liter of hydrogen peroxide are as follows.

	g./liter
For methyl cyclohexanol acetate	2.8
For dimethyl cyclohexanol succinate	1.9

Thus, clearly the solubility of the quinhydrone is less in the mixture containing the succinate than in the mixture containing the acetate.

A further and most important factor favoring the methyl cyclohexanol acetate is that it is available at a reasonable price commercially, whereas the dimethyl cyclohexanol succinate is not available commercially, and if it were it would be likely to be of higher price than the acetate.

Aromatic Alcohols and Their Esters

FMC; Käbisch, G. and Richter, E. (10): It is claimed that certain aromatic alcohols and their esters possess many of the desired properties of an ideal solvent for use in the anthraquinone process. This fact is quite surprising, since previously the aliphatic and alicyclic alcohols and their esters were emphasized as being particularly suitable solvents.

The aliphatic and alicyclic alcohol solvents until now used in industry have been found to dissolve the anthrahydroquinones in sufficient quantity, but to fail as solvents for the anthraquinones. However, the specified aromatic solvents have the advantage that they not only dissolve large amounts of the anthrahydroquinone, which would be predicted from their chemical natures, but also that they dissolve the anthraquinones in sufficiently large quantities, as can be seen from the following table of comparison:

Solvent	Grams ethylanthraquinone per 100 ml. solvent, 20° C.
Prior art solvents:	
(1) Ethyl alcohol	0.8
(2) Heptanols—nonanols	2-3
(3) Cyclohexanol acetate	4.1
Solvents of this invention:	
(4) Benzyl alcohol	17
(5) β-phenylethyl alcohol	16.5
(6) β-phenylethyl acetate	17.6
(7) β-phenylethyl propionate	12.5
(8) Methoxyphenylethyl acetate	8.5
(9) Tolylethyl isobutyrate	14.3

The term aromatic alcohols and their esters means compounds which consist of a suitably substituted benzene ring or naphthalene unit with one or several side chains that have at least one alcohol group which in turn may be esterified. The length of any side chain shall not be more than 10 carbon atoms, since otherwise the viscosity of the compound will become too great. The β-phenylethyl alcohol and the β-tolylethyl alcohol, their esters, and their simple derivatives, are particularly effective.

Since the solvents are suitable for dissolving both the anthraquinone and the anthrahydroquinone forms of the working compound, they can be used as a sole solvent in the anthraquinone process. This permits simplification in the makeup of the working solution.

Additional advantages possessed by the solvents are their high melting points and flash points, and their excellent hydrogen peroxide distribution coefficients, that is the ease with which hydrogen peroxide can be separated from them. The above solvents also can be used advantageously in admixture with other solvents, and are likewise suited for use with other working compounds besides ethylanthraquinone, for example with other alkylated anthraquinones, e.g., tertiary butyl anthraquinone, or anthraquinones having one or more alkyl groups, or with halogenated anthraquinones.

Ring-Alkylated Acetophenones

FMC; Richter, E., Gross, A., and Käbisch, G. (11): According to German patent application No. A 21273 IVa/12i, certain ketones are suggested as single solvents for the quinone form as well as the hydroquinone form of the working material. The compounds referred to in the cited German patent application are the ketones in which the hydrocarbon groups next to the carbonyl group contain at least two carbons, as for example, diethyl ketone, diisopropyl ketone, or diisobutyl ketone. The solubility of 2-ethylanthraquinone, for example, at 20°C. and in diisopropyl ketone, and in diisobutyl ketone, is stated to be 8.5% and 6% respectively. Corresponding solubilities of the 2-ethylanthrahydroquinone are said to be equal to these values or somewhat larger.

It has now been found that a considerably better dissolving effect for both the quinone and hydroquinone forms can be provided if as sole solvent or as a solvent constituent in a solvent system, a methyl ketone of the general formula CH_3-CO-R is used, where R represents a suitably singly or multiply substituted phenyl, napthyl or cyclohexyl group. Particularly suitable as solvents, are the singly or multiply, nuclearly, alkyl-substituted and chloro-substituted acetophenones in which R is a substituted phenyl group.

The solvents have high boiling points and therefore low losses through evaporation in a continuous process, high flash points, low solubilities in water, and high distribution coefficients, relative to water, of the hydrogen peroxide formed in the anthraquinone process. They are neither reduced nor oxidized under the reaction conditions that exist in the anthraquinone process. The unsubstituted acetophenone, despite its excellence as a solvent for the anthraquinones and their hydro derivatives, is not suited for use as a solvent in the anthraquinone process because of its density of 1.026, which is close to the density of water. This makes it difficult to separate the hydrogen peroxide-containing water phase from the quinone phase extraction of the peroxide from the working solution with water. Accordingly, it is preferred to employ a solvent having a density of at least about 0.03 removed from the density of water, namely, having a density of less than 0.97 or greater than 1.03. This permits ready extraction by water of the hydrogen peroxide that forms in the anthraquinone process.

Regarding the densities of the solvents now proposed it was found that by the nuclear substitution of one or more alkyl groups into the ring groups in the solvents, for example by the substitution of one or more alkyl groups containing a total of 4 to 9 carbon atoms onto the phenyl nucleus of the acetophenone, or by the substitution of one or more alkyl groups containing a total of 1 to 4 carbons onto the cyclohexane or naphthalene radical of the cyclohexyl ketone or the naphthone, respectively, a solvent was provided which has a density lower than about 0.97, and which also has the other properties required for the anthraquinone process. Thus, for example, p-tertiarybutyl acetophenone has a density of 0.962

compared with the density of 1.026 possessed by unsubstituted acetophenone. This alkylated acetophenone has a dissolving power for 2-ethylanthraquinone and 2-ethylanthrahydroquinone which is typical of the solvents of this process, being capable of dissolving more than about 19% of the anthraquinone form, and more than about 8% of the hydroquinone form, and further is highly insoluble in water. It likewise has been found that substitution of one or more halogens in the ring nucleus raises the density of the solvent as compared to the unsubstituted parent compounds. Thus, for example, ortho or p-chloroacetophenone has a density of 1.188.

The following is a list of solvents which fall within the scope of this process: the nuclearly chlorinated and dichlorinated acetophenones; 2-methyl-5-isopropyl-acetophenone; p-tertiarybutyl-acetophenone; 2,4-dimethyl-4-ethyl-acetophenone; tetramethyl-acetophenone; 2-methyl-4-tertiarybutyl-acetophenone; dipropyl-acetophenone; 2,4-dimethyl-6-ethyl-tertiarybutyl-acetophenone; 2,4,6-trimethyl-diethyl-acetophenone; n-octyl-acetophenone; 5-methyl-2-n-octyl-acetophenone; α-chloro-acetonaphthone; 1-methyl-acetonaphthone; 4-ethyl-acetonaphthone; 2,6-dimethyl-acetonaphthone; 1-methyl-4-ethyl-2-naphthone; chlorinated methyl-cyclohexyl-ketone, and methyl-hexahydroacetophenone.

Diisobutylketone

Societe d'Electrochimie, d'Electrometallurgie et des Acieries Electriques d'Ugine and l'Air Liquide; Villemey, L. (12): The object of this process is the use, as solvents, of certain ketones which have been found as nonhydrogenable under normal conditions in which anthraquinone may be hydrogenized. Ketones being generally considered as hydrogenizable substances, their use as a nonreactive solvent for the hydrogenation of anthraquinones was unexpected.

The ketones in question are the ones in the molecule of which each of the radicals adjacent the carbonyl group comprises at least two carbon atoms; among these ketones, the most convenient are those having an oxidizing power (defined according to Cox and Adkins, J. Am. Chem. Soc., 61, 3369, 1939, with respect to that of diisopropylketone taken as a reference and set equal to unity) equal to or larger than 0.6. Further, they do not form stable peroxides and show other characteristics required for a solvent used as a vehicle for quinone in the application of the above process. As examples may be mentioned diethylketone, diisopropylketone, diisobutylketone, etc. These ketones show particular advantages as vehicles for anthraquinone in hydrogen peroxide making. The properties required for such solvents are nonsolubility in water, chemical stability, a dissolving power both for the quinone form and the hydroquinone form, a high distribution factor of hydrogen peroxide in water vs. the solvent, a density sufficiently different from that of water, etc.

The ketone may be either the single constituent in the solvent or admixed with another known solvent, as for instance hydrocarbons such as alpha-methylnaphthalene, beta-methylnaphthalene, dimethylnaphthalene, ditolylethane, etc.; alcohols like n-heptanol, octanol, lauric alcohol, etc.; ether-oxides like anisole, phenyl-oxide, etc.; esters like n-heptylacetate, ethylheptanoate, heptylheptanoate, etc.

A specially interesting solvent is diisobutylketone. Its specific gravity at 20°C. compared with the one of water at 4°C. (D_4^{20}) is 0.8063. The solubility of diisobutylketone in

water is 0.064 g. in 100 g. at 20°C. The solubility of water in diisobutylketone is 0.45 g. in 100 g. at 20°C. The following is an example of its application in the anthraquinone process.

A solution of 2-ethylanthraquinone in diisobutylketone is used. Solubility of ethylanthraquinone in diisolbutylketone at 20°C. is 6%. The distribution factor of hydrogen peroxide between water and the saturated solution of ethylanthraquinone in the solvent is 1:49. The solubility of 2-ethylhydroanthraquinone in diisobutylketone at 20°C. is equal to or larger than 6%. The separation between water or hydrogen peroxide and the solution of ethylanthraquinone in diisobutylketone is quite sharp, so that decantation is very easy.

Further, the rate of hydrogenation of 6% solution of ethylanthraquinone and the rate of reoxidizing of the hydrogenated solution are particularly high owing to low viscosity of the same. It will also be noted that, contrary to the case of solutions of alkylanthraquinone in usual solvents, solubility of the hydroquinone form is as high as solubility of the quinone form; this makes it possible to completely avoid precipitation of anthraquinone when effecting the complete hydrogenation of a saturated solution of the anthraquinone.

Ethyl Benzoate

Montecatini; Cubeddu, T. (13): According to this patent, the anthraquinone process can advantageously be carried out by employing an alkyl ester of benzoic acid as solvent. Such solvents are most suitable here, since they dissolve both the quinonic form and the hydroquinonic form. Ethyl benzoate is preferred.

By using a solvent of this type, it is possible to utilize the dissolving power for both forms of the alkylanthraquinone most advantageously. Since the highest amount of the same solvent is always available for both forms, the solvent is always available in the process. The solvent has a high solvent power in comparison with other solvents or mixtures of solvents which are described in the prior patents. The process results in high concentrations of hydrogen peroxide, and has a marked advantage in this respect over the other solvent mixtures of the prior art.

The alkylester of benzoic acid can be used in admixture with other specific solvents, either for the quinonic or for the hydroquinonic form. Thus the process can be modified to accommodate it to the characteristics of the particular alkylanthraquinone utilized, or to the special working conditions employed. The following example is illustrative; other alkylanthraquinones can be utilized.

20 g. 2-ethylanthraquinone are dissolved in 100 cc. ethyl benzoate, thus obtaining 116 cc. of solution. The solution is hydrogenated in the presence of Raney nickel with 1,242 cc. hydrogen, calculated at 0°C. and 760 mm. Hg. Upon oxidation of the solution and subsequent extraction with water, 1.86 g. H_2O_2 are obtained. Therefore, there is a concentration of 16 g. H_2O_2 per liter in the organic solution. The yield of H_2O_2 calculated on the basis of introduced hydrogen appears to be 98%.

Polyalkylated Benzene/Trisubstituted Organic Ester of Phosphoric Acid Mixture

FMC; Käbisch, G. (14): It has been found that a solvent mixture consisting essentially of a polyalkylated benzene having 9 to 11 carbon atoms and a trisubstituted organic ester of phosphoric acid, the former being the solvent for the anthraquinone form of the working compound and the phosphoric acid ester being the solvent for the anthrahydroquinone form of the working compound, is a highly effective solvent combination which satisfies essentially all of the requirements for an ideal solvent in the anthraquinone process.

This polyalkylated benzene – organic phosphoric acid ester combination preferably contains about 60 to 85 volume percent of the polyalkylated benzene and about 40 to 15 volume percent of the phosphoric acid ester, and is used in the amount of at least about 37.5 volume percent of the total volume of the work solution.

The polyalkylated benzenes in the mixtures are benzenes carrying alkyl substituents and having a total of 9 to 11 carbon atoms. These compounds may be the trimethyl, methylethyl, methylbutyl, tetramethyl and the like benzenes. The compounds are available in the form of individual isomers or of mixtures of isomers, as well as in admixtures containing various compounds within the defined class. Likewise, they are frequently obtained in mixtures comprising from about 70% up to substantially 100% of the polyalkylated benzene, with the balance largely being paraffinic compounds having roughly the same boiling temperatures as the boiling temperatures of polyalkylated benzenes, namely about 145°C. to 320°C. When they are used in such mixtures, the volume percentages of the polyalkylated benzenes are calculated on the basis of the amounts of these compounds present relative to the phosphoric acid ester, not taking into account the amount of paraffin hydrocarbon present.

Typical polyalkylated benzene solvent compositions in which mixtures of various class compounds and paraffinic compounds are present, are Solvents A and B. These solvents have the following compositions:

Ingredient:	Volume percent
Solvent A—	
1,3,5-trimethylbenzene	15
1,2,4-trimethylbenzene	43
1,2,3-trimethylbenzene	12
1-methyl 4-ethylbenzene	2
1-methyl 3-ethylbenzene	6
1-methyl 2-ethylbenzene	2
Paraffins	20
Solvent B—	
Dimethylethyl and tetramethylbenzenes	71
C–11 alkylated benzenes	22
Paraffins	7

These compounds are derived most suitably from petroleum, and then are particularly useful, because of their low contents of sulfur and other poisons, for the hydrogenation catalysts used in the anthraquinone process. The compounds are derived by catalytic reformation of desulfurized straight run benzines, for example through aromatizing aliphatics, dehydrogenating naphthenes, and cracking and aromatizing of the heavy components of the straight run benzine.

The trisubstituted organic esters of phosphoric acid, used as solvents for the anthrahydroquinone form of the working compound, are phosphates on which there are three hydrocarbon substituents, which substituents may be alkyl or aryl groups. Typical useful phosphates are trioctylphosphate, tributylphosphate, diphenyloctylphosphate, diphenylcresylphosphate and tricresylphosphate. These phosphates and their use in the anthraquinone process are described in U.S. Patent 2,537,655 to Dawsey et al. The following table shows the solubility of 2-ethylanthrahydroquinone in various phosphates from this class:

Solvent:	Grams of 2-ethylanthrahydroquinone soluble in a liter of solvent at 25° C.
Tributylphosphate	366
Trioctylphosphate	202
Diphenylcresylphosphate	136
Diphenyloctylphosphate	165
Tricresylphosphate	154

The ratio of anthraquinone solvent to anthrahydroquinone solvent may be varied within reasonably broad limits, and other solvents and/or inert substances may be added to the solvent mixture. Particularly useful solvent combinations are those in which the ratio of anthraquinone solvent to anthrahydroquinone solvent, that is of the polyalkylated benzene to the phosphoric acid ester, is about 60 to 85 volumes of the former to 40 to 15 volumes of the latter. These solvents are used in the working solution in an amount of at least about 37.5% by volume, that is in an amount to provide at least about 15% by volume of the phosphoric acid ester. Use of less solvent causes the resulting working solution to have properties which make it difficult to process. The maximum amount which may be used is dictated by economic considerations. It is obvious that use of too much solvent reduces the amount of reactive working compound which may be present.

It is possible to use the quoted amounts of the substituted phosphate for the reason that these materials dissolve unusually large amounts of anthrahydroquinones, such that a liter of a solvent mixture consisting of 75 volume percent of trimethylbenzene and only 25 percent by volume of trioctylphosphate at a temperature of 20°C. dissolves more 2-ethylanthrahydroquinone than do solvent mixtures of the same trimethylbenzene with two typical prior art solvents for anthrahydroquinones, namely diisobutylcarbinol and methylcyclohexanol acetate in which the anthrahydroquinone solvent is present in the amount of one-half rather than 25%, or one-fourth, of the total solvent mixture. This is shown in the following table.

Solvent Mixture	Maximum solubility of 2-ethylanthrahydroquinone (g./l. of solvent) at—		
	20° C.	30° C.	40° C.
75% by vol. trimethylbenzene, 25% by vol. trioctylphosphate	60	62	64
50% by vol. trimethylbenzene, 50% by vol. diisobutylcarbinol (comparative)	40	42	44
50% by vol. trimethylbenzene, 50% by vol. methylcyclohexanol acetate (comparative)	44	45	46

Accordingly, the particular solvent mixture of this process has an unusual ability to dissolve

the anthrahydroquinone form of the working compound, such that the polyalkylated benzene component which is the anthraquinone solvent can be correspondingly increased in amount, thereby minimizing the danger of work compound crystallizing out of the working solution when it is in the anthraquinone form, and also providing a higher yield of hydrogen peroxide per unit volume of reaction equipment.

All of the currently used anthraquinone working compounds, namely the substituted anthraquinones, may be employed with the new solvent mixtures. Thus the alkylanthraquinones, the anthraquinone carboxylic acid esters, the anthraquinone sulfonic acid esters, the halogenated anthraquinones and other prior art anthraquinones used in the anthraquinone process are useful with the present solvent mixtures. Particuly useful anthraquinones are 2-ethylanthraquinone, tetrahydroethylanthraquinone, tert.-butylanthraquinone and amylanthraquinone. Their solubilities in terms of grams of the anthraquinone soluble per liter of a typical polyalkylated benzene of this process, namely Solvent A, are as follows:

Anthraquinone Derative	Grams Soluble in a Liter of Solvent A		
	20° C.	30° C.	40° C.
Ethylanthraquinone	200	260	322
Tetrahydroethylanthraquinone	187	196	218
Tert.-butylanthraquinone	480	598	755
Amylanthraquinone	214	296	444

The previously used anthraquinone solvents from the naphthalene class, particularly the α- and β-monomethylnaphthalenes and the dimethylnaphthalenes, show similar or even slightly better dissolving powers for the anthraquinones. However, use of the naphthalene compounds in the anthraquinone process gives rise to poisoning of the hydrogenation catalyst due to the derivation of these materials from tar distillation fractions which contain catalyst poisons. Costly preliminary purification of the naphthalene therefore is necessary, whereas in the case of the polyalkylated benzenes it is avoided. Furthermore, a comparison of the viscosity and density values for the trimethyl benzenes such as Solvent A, and dimethylnaphthalene, shows that the dimethylnaphthalene has a density very close to that of water, so that it is difficult to separate it from water in the hydrogen peroxide extraction step; also it has a very high viscosity in comparison with the trimethylbenzene, which makes it difficult to cycle a working compound containing it through the reaction equipment. The following table demonstrates this difference in properties:

Property	Solvent A	Dimethylnaphthalene
Density at 20° C. (water is 1.0)	0.875	0.999
Viscosity at 20° C. in cp	.59	3.50

Use of Solvent A, having these properties, translated into the following practical operating advantages over use of dimethylnaphthalene. The height of the extraction column required to extract hydrogen peroxide from a typical working solution containing the Solvent A was about 15% less than the column length required when dimethylnaphthalene was used.

Further, it was possible to put through a reactor column having the same height and cross-sectional area, 25% more working solution employing the Solvent A polyalkylated benzene than was possible when employing dimethylnaphthalene. Incidentally, foam formation in the oxidation stage was reduced with Solvent A; separation of the hydrogenation catalyst accordingly was facilitated where suspension catalysis was employed.

Table 2.2 presents important physical properties of four typical polyalkylated benzene solvents together with those for a comparative solvent, dimethylnaphthalene. This table presents the densities, refractive indices, viscosities and boiling temperature ranges for these various solvents, and additionally shows the solubility of 2-ethylanthraquinone at 20°, 30° and 40°C. in grams of the ethylanthraquinone soluble per liter of the indicated solvents.

TABLE 2.2: ANTHRAQUINONE SOLVENTS

	Solvent A	Solvent B	1,3,5-trimethylbenzene	1,2,4-trimethylbenzene	Dimethylnaphthalene
Density D_4^{20}	0.875	0.889	0.8651	0.8758	0.999
Refractive Index n_4^{20}	1.504	1.5106	1.499	1.505	1.602
Viscosity at 20° C. in cp	0.59	1.18		1.00	3.5
Boiling Range at 760 mm. Hg	158–186	184–202	163–165	169	249–262
Sol. EAQ,* g./l. solvent:					
20° C	200	226	200	249	280
30° C	260	358	261	324	375
40° C	322	476	350	419	500

*2-ethylanthraquinone.

The densities and viscosities of working solutions prepared with the polyalkylated benzene solvents are correspondingly better in each case than the densities and viscosities of such working solutions prepared with the dimethylnaphthalene, and all of these solvents have highly satisfactory dissolving powers for the ethylanthraquinone. The following example is presented by way of illustration of this process.

One hundred and thirty grams of 2-ethylanthraquinone was dissolved in a solvent mixture consisting of 25 parts by volume of trioctylphosphate and 75 parts by volume of Solvent A (polyalkylated benzenes). The working solution provided thereby was exposed to hydrogen in a hydrogenation apparatus in the presence of a fluidized palladium black catalyst at a temperature of 45°C., at a solution flow of 500 liters of solution per hour and a gas flow of 2,580 liters of hydrogen per hour. The hydrogen uptake corresponded to a 46% hydrogenation of the anthraquinone present, and an almost quantitative uptake of the hydrogen. The hydrogenation catalyst was separated by filtration, and the hydrogenated solution was oxidized at 43°C. with an amount of air to provide an excess of 30% over the amount required for the oxidation. There was produced 8.6 grams of hydrogen peroxide per liter of working solution. This hydrogen peroxide was extracted with water in an extraction column, and the organic phase returned to the hydrogenator for further cycling.

WORKING SOLUTIONS

In this section, there follow two novel combinations of working materials and working solvents, and a process for preventing poisoning of the hydrogenation catalyst.

Alkylated Anthraquinones in Organic Phosphate Esters

FMC; Darbee, L.B., and Conroy, P.G. (15): This process deals with means for improving the solubility of the working compound by employment of particular alkylated anthraquinones and their tetrahydro derivatives in specified amounts of solvent, all to the end that the concentration in unit volume of working solution may be enhanced.

The particular advantages of the process are obtained by employing as the working compound either 2-secondary butylanthraquinone or 2-isopropylanthraquinone, as these two alkylated anthraquinones possess a particular characteristic as to solvency which appears not to be possessed by the other usually employed alkylated anthraquinones, namely, the methyl, ethyl or tertiary butyl compounds.

The hydroquinone forms of methyl, ethyl and tertiary butyl anthraquinones exhibit substantially no solvency in those solvents which have heretofore been designated quinone solvents. The quinone form of methyl, ethyl and tertiary butyl anthraquinone exhibit much less solvency than their hydroquinone forms in solvents so far designated as hydroquinone solvents. It has now been found that this relationship in hydroquinone solvents is reversed in the case of the 2-secondary-butyl and 2-isopropyl substituted compound. This relationship is strikingly shown in the table below, where the figures given represent the number of grams of the indicated alkylated material soluble in 10 cc. of the specified solvent at 25°C., where "Q Form" represents the quinone form and "HQ" the hydroquinone form of the specified alkylated anthraquinone.

Alkylated Anthraquinone	Trioctyl Phosphate		Tri-n-butyl Phosphate		Tri (2-ethylbutyl)[b] Phosphate	
	Q Form	HQ Form	Q Form	HQ Form	Q Form	HQ Form
2-methyl	0.1	1.75	0.1	2.80	0.1	1.60
2-ethyl	0.40	2.06	0.57	3.36	0.45	1.85
2-tertiarybutyl	0.93	2.80	1.2	4.33	0.91	2.44
2-secondarybutyl	3.16	1.89	5.5	3.3	3.77	1.73
2-isopropyl	2.6	1.48	4.35	2.43	2.86	1.58

Reference to the above table will show that 2-tertiary butylanthraquinone, in the three specified organic phosphate esters normally considered as solvents for the hydroquinone form of the working material, possesses the normal solubility characteristic expected, namely, a substantially greater solubility of the hydroquinone form than of the quinone form. In this respect, the tertiary butylanthraquinone behaves in the same fashion as the methyl derivative and the ethyl derivative. Thus the solubility of 2-tertiary butylanthraquinone in tri-n-butyl phosphate is 1.2 g. in 10 cc. at 25°C., whereas that of tertiary butylanthrahydroquinone is 4.33 g. in 10 cc. of that solvent at the same temperature, a solubility advantage of more than 3 1/2 times with respect to the hydroquinone form.

When considering the solubility of secondary butyl anthraquinone however, in the same solvent, the quinone form of that material is 5.5 g. in 10 cc. of tri-n-butyl phosphate and the solubility of the hydroquinone form is less, being only 3.3 g. in 10 cc. of that solvent at 25°C. This same relationship of solubility exists in the other solvents listed, which are thought of in the art as being solvents for the hydroquinone form of the working material. The same reversed relationship exists when considering isopropyl anthraquinone.

In the process, considerable advantage in concentration of working material is obtained when the working solution is made up from either secondary butylanthraquinone, isopropyl-anthraquinone or mixtures thereof, and particularly the eutectic mixture, and to employ either a mixed solvent or a single solvent, the essential major constituent of which is an organic ester of phosphoric acid. This same apparent reversal of solubility has been found to be present in the case of the generally employed C-7 to C-11 aliphatic alcohols, as for instance the nonyl alcohols, alkyl cyclohexanols and phosphonate esters, all previously considered as solvents for the hydroquinone form of the working material.

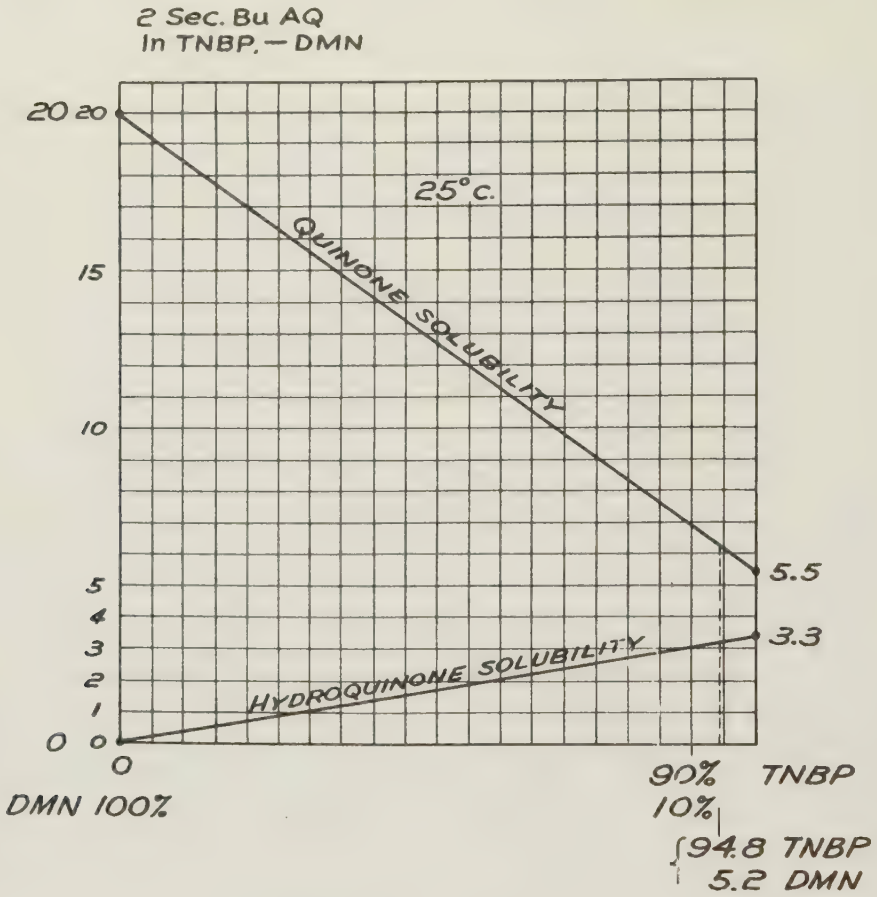
A simplified concept of the advantages of the process may be obtained by considering the solubility of the quinone form and hydroquinone form of secondary butyl anthraquinone in tri-n-butylphosphate. Under an operating temperature of 25°C., 100 cc. of tri-n-butyl phosphate would carry in solution 55 g. of the quinone form of working material and therefore no additional solvent need be employed to carry the product produced in the hydrogenation step of the anthraquinone process, provided the hydrogenation is not carried further than 60% (33/55 X 100).

The table below sets forth the solubility in grams of the indicated alkylated anthraquinone in dimethylnaphthalene, a solvent representative for dissolving the quinone form of the working material, and presently considered of particular advantage in the mixed solvent process.

Alkylated Anthraquinone	Dimethylnaphthalene	
	Quinone Form	Hydroquinone Form
2-methyl	.78	0.0
2-ethyl	3.20	0.0
2-tertiary butyl	5.9	0.0
2-secondary butyl	20.0	0.0
2-isopropyl	27.0	0.0

Figure 2.3 shows the solubility of 2-secondary butylanthraquinone in tri-n-butyl phosphate and dimethylnaphthalene mixtures. It will be noted that the hydroquinone form is insoluble in dimethylnaphthalene, that is 0.0 gram, and is soluble to the extent of 3.3 grams in 10 cc. of tri-n-butyl phosphate, while the quinone form of the secondary butyl derivative is soluble to the extent of 20 g. in 10 cc. of dimethylnaphthalene at 25°C. and to the extent of 5.5 g. in 10 cc. of tri-n-butyl phosphate. A working solution containing 94.8% by volume of tri-n-butyl phosphate and 5.2% by volume of dimethylnaphthalene will carry as working material 6.24 g. 2-secondary butyl anthraquinone in 10 cc. Hydrogenating to 50% produces no cloud, so that all the hydroquinone forms thereby produced remained soluble.

FIGURE 2.3: SHOWING THE SOLUBILITY OF 2-SECONDARY BUTYLANTHRAQUINONE IN TRI-N-BUTYL PHOSPHATE AND DIMETHYLNAPHTHALENE MIXTURES



Source: L.R. Darbee, P.G. Conroy, U.S. Patent 2,935,381, May 3, 1960

On subsequent oxidation and water extraction of the working solution, a yield of hydrogen peroxide of 0.267 g. is obtained – a yield equivalent to 26.7 g. per liter of working solution. This is in contrast to a yield of 5.5 g. hydrogen peroxide per liter in the commercial operation described in PB Report 4336, of 11 g. per liter as shown in U.S. Patent 2,689,169, and 11.3 g. per liter as shown in U.S. Patent 2,768,066.

A singular advantage of the process, as will be seen from above, resides in the very material reduction in amount of solvent and accompanying increase in amount of working material capable of being carried and operated upon for the production of hydrogen peroxide through the hydrogenation cycle, while maintaining each of the quinone form and hydroquinone form in solution thereby increasing the production capacity of a given installation which consists of, in broad aspect at least, a hydrogenating chamber or column, an oxidizing chamber or column and an extracting chamber or column or peroxide extractor where the hydrogen peroxide is extracted with water.

In the experimental data above, results have been shown in systems employing tri-n-butyl phosphate as the hydroquinone solvent and dimethylnaphthalene as the quinone solvent. It will be understood that comparable results can be obtained by using mixtures of solvents known as hydroquinone solvents or mixtures of solvents known as quinone solvents instead of the single species of each class as illustrated above.

Additional data are shown below for various systems in which the yield of hydrogen peroxide is indicated at various depths of hydrogenation. There is also given the volume fraction of the working solution of specified solvent for the hydroquinone form. In the instances shown below, the solvent is constituted of diisobutyl carbinol and alphamethylnaphthalene. The solubility of secondary butylanthraquinone in 10 cc. of the specified solvent is given in the table below.

Compound	Solvent	Solubility
Secondary butylanthraquinone.	alpha-methyl naphthalene	22.7 g. in 10 cc.
Do	di-isobutyl carbinol	1.95 g. in 10 cc.
Secondary butylanthra-hydroquinone.	alpha-methyl naphthalene	0.0 g. in 10 cc.
Do	di-isobutyl carbinol	1.43 g. in 10 cc.

When secondary butylanthraquinone is employed in a mixed solvent of alphamethylnaphthalene and diisobutyl carbinol and the solution designated worked at maximum capacity at 30°C., for the selected degree of hydrogenation, the following yields of hydrogen peroxide are obtained:

Depth of Hydrogenation in Percent of Complete Hydrogenation	Volume Fraction Di-isobutyl Carbinol	Yield Hydrogen Peroxide, Grams H_2O_2 per liter
20	0.813	10.2
30	0.889	12.2
40	0.983	13.5
50	0.962	14.5
60	0.981	15.2
70	0.996	15.8
80	1.00	16.1

In the same manner, isopropyl anthraquinone worked in a mixed solvent of dimethylnaphthalene and tri-normal butyl phosphate, if worked at maximum capacity of 25°C. for the selected depth of hydrogenation indicated, also shows exceptional yield of hydrogen peroxide. The solubility data is as follows:

Compound	Solvent	Solubility
Isopropylanthraquinone	Dimethylnaphthalene	27.0 g. in 10 cc.
Do	Tri-normal butyl phosphate.	4.35 g. in 10 cc.
Isopropylanthrahydroquinone	Dimethylnaphthalene	0.0 g. in 10 cc.
Do	Tri-normal butyl phosphate.	2.30 g. in 10 cc.

Depth of Hydrogenation in Percent of Complete Hydrogenation	Volume Fraction Tri-normal butyl Phosphate	Yield Hydrogen Peroxide, Grams H_2O_2 per liter
20	.776	14.4
30	.879	18.4
40	.940	21.2
50	.982	23.3
60	1.00	24.9
70	1.00	25.8
80	1.00	26.5

In like manner, the system 2-secondary butylanthraquinone as the working compound in a working solution of dimethylnaphthalene and tri(2-ethyl hexyl)-phosphate, worked to maximum capacity at 25°C. at the various selected depths of hydrogenation, give the following results:

Compound	Solvent	Solubility
Secondary butylanthraquinone.	Dimethylnaphthalene	20.0 g. in 10 cc.
Do	Tri-octyl phosphate	3.16 g. in 10 cc.
Secondary butylanthrahydroquinone.	Dimethylnaphthalene	0.0 g. in 10 cc.
Do	Tri-octyl phosphate	1.89 g. in 10 cc.

Depth of Hydrogenation in Percent of Complete Hydrogenation	Volume Fraction Tri-octyl Phosphate	Yield Hydrogen Peroxide, Grams H_2O_2 per liter
20	.761	11.7
30	.865	14.5
40	.929	16.7
50	.970	18.2
60	1.00	19.4
70	1.00	20.0
80	1.00	20.4

2-Tert.-Amylanthraquinone and 2-Iso-sec.-Amylanthraquinone Mixture in Benzene/Aliphatic Alcohol Solvent Mixture

Hiratsuka, K. et al (16): The novelty of this process comprises employing as alkylanthraquinone an amylanthraquinone mixture consisting of 2-tertiary-amyl-anthraquinone and 2-iso-secondary-amylanthraquinone at a ratio of 50 to 95% by weight of the former to 50 to 5% of the latter; and using as solvent mixture a first solvent selected from the group consisting of benzene, alkyl substituted benzene and alkyl substituted naphthalene, and a second solvent selected from the group consisting of aliphatic alcohols having from 7 to 11 carbon atoms and alkylcyclohexanol, in a volume ratio range between first and second solvent of about 40-60:60-40.

Working Solution Is Freed from Residual H_2O_2 by Use of Stannous Salts, thus Preventing Poisoning of Raney Nickel Hydrogenation Catalyst

Kali-Chemie AG; Hauschild, U. (17): Hydrogenation of the quinone is carried out in the presence of a known metal-hydrogenation catalyst. Palladium applied to a carrier material, such as aluminum oxide, magnesium oxide, calcium carbonate, calcium phosphate, or Raney nickel, are generally used. These catalysts possess, prior to their introduction into the hydrogenating device, a definite activity which can be tested according to known methods.

In the course of a continuous process, the activity of the hydrogenating catalyst decreases more or less, so that fresh catalyst has to be added continuously. The loss of activity is due primarily to the presence of quite specific catalyst poisons. If these catalyst poisons cannot be completely or almost completely eliminated, considerable expenses for the catalyst may occur. It has been known that H_2O_2 is a strong catalyst poison for Raney nickel already at very low concentrations. It is, therefore, desirable to exclude the presence of this catalyst poison when a Raney nickel hydrogenation catalyst is used. It is known that in the cyclic process after the oxidation step the operating solution is extracted with water in order to remove all H_2O_2 as far as possible. However, due to the distribution equilibrium between organic and aqueous phase, it is not possible to extract the last parts of H_2O_2, and by the latter a continuous decrease of activity of the Raney nickel is caused.

For this reason, various suggestions have been already made to remove the H_2O_2 which is still present in small quantities in the operating solution, prior to the hydrogenation step. It has been known, for example, that H_2O_2 can be catalytically decomposed by various heavy metals, such as iron, nickel, copper, or noble metals such as platinum or palladium. The corresponding metal oxides and hydroxides act also in a similar manner. The essential drawback of this treatment consists in that the liberated oxygen can react with hydroquinone still present in the solution with renewed formation of H_2O_2.

Treatment with solid substances or substances dissolved in water, which are capable of binding H_2O_2, such as sodium hydroxide, sodium metaborate or sodium carbonate has likewise been known. However, the efficiency of this treatment – which is often accompanied by a chemical change of the cycled organic solution – is very low, because considerable parts of H_2O_2 still remain in the organic solution. It has also been suggested to treat the organic solution with mangano- and ferro-compounds, e.g., with a solution of $FeSO_4$ or with alcoholic solutions or suspensions which contain $Fe(OH)_2$. Thereby oxygen, which is eventually dissolved in the solution, is also supposed to be removed, because these compounds are easily oxidized particularly in alkaline solution. However, apart from the consumption of chemicals, this suggestion is also not satisfactory because it can relatively easily happen that iron or manganese enters the organic solution, so that decompositions occur in the oxidation step.

It has now been found, that the above described disadvantages can be avoided and a total removal of H_2O_2 which remains in the operating solution of the anthraquinone process can be attained prior to the hydrogenating step by treating the organic solution with an aqueous solution of a stannous salt. It is surprising that stannous salt solutions remain practically indifferent to the anthraquinone solutions during the short period of time which is necessary for the extraction and react with the H_2O_2 only. Operation at ordinary room temperature is preferred. In carrying out the process, it is further preferred to use the stannous chloride, although other water-soluble stannous salts, e.g., the sulfate or fluoride, can also be used.

Concentration of the stannous salts in the aqueous phase may have any desired value. It depends primarily on the amount of H_2O_2 still present in the organic solution, because in order to completely remove the H_2O_2 an excess of the respective stannous salt must always be, of course, available. As a rule, solutions containing 1 to 5% of the stannous salts are used. By the addition of a small amount of a mineral acid, precipitation of oxy compounds, or hydroxide or oxide, can be prevented, in order to avoid disturbances during the fluid-fluid extraction. Moreover, adjustment of the aqueous phase to a low pH has a rather favorable influence on the separation of the organic and aqueous phase after extraction, so that an undesired formation of emulsions is avoided.

A particular advantage of using stannous salt solutions for the removal of small amounts of H_2O_2 from the organic solutions of the anthraquinone process consists in the possibility of easy regeneration of the stannic salt solutions formed. For example, a $SnCl_4$ solution can be electrolytically reduced to a $SnCl_2$ solution in conventional manner. An aqueous $SnCl_2$ solution can be used, therefore, in a cycle permanently, by bringing it first in contact with the organic solution in order to remove residual amounts of H_2O_2, then separating it and finally subjecting it to treatment in an electrolytic device for reducing the stannic formed. It will be understood that the Sn salt solution can be regenerated also by other reducing agents

The operating solutions which are used in the production of H_2O_2 according to the anthraquinone process, still contain, prior to their entering into the hydrogenating apparatus, parts of hydrogenated anthraquinone compounds. Because these compounds are capable of reacting with oxygen with the formation of the corresponding quinone compounds and H_2O_2, it is advisable to exclude the access of oxygen during and after the treatment with the stannous compounds by the use of an inert gas atmosphere, preferably nitrogen. Furthermore, the solution can be aerated with nitrogen prior to the treatment in order to remove oxygen dissolved in the solution. The following example describes a suitable way for carrying out the process.

A solution of 60 grams of ethylanthraquinone in 500 ml. of benzol and 500 ml. of octanol was stirred at 40° to 50°C. with hydrogen in the presence of Raney nickel until about half of the amount of ethylanthraquinone, which could be theoretically expected, was formed. After separation of the catalyst, the solution was completely oxidized by blowing in air and 4 grams of H_2O_2 were thereby formed. Subsequently extraction was carried out five times with 50 ml. of water in each case.

After this treatment, the organic solution still contained 25 mg. of H_2O_2. In order to remove air dissolved, nitrogen was introduced into the solution by means of a glass frit. The solution was now extracted with 50 ml. of an aqueous $SnCl_2$ solution which contained 3 grams of $SnCl_2$ in 100 ml. and to which a few drops hydrochloric acid were added previously. After the two phases were separated, no H_2O_2 could be found any more in the organic solution.

REGENERATION OF WORKING SOLUTION

By Treatment with Alkali Metal Hydroxide

Solvay & Cie; Denaeyer, J.L., and Jones, R. (18): As stated before, in the anthraquinone process for H_2O_2, continuous recycling of the working solution causes the formation of decomposition products of alkylanthraquinones. Some of these products are inert, i.e., unfit for the production of hydrogen peroxide. Their presence in the recycle solution is the cause of many disadvantages, among which may be mentioned the need for periodic addition of fresh quinone to compensate for that rendered inactive by decomposition, in order to maintain the production capacity of the plant. This causes an increase in the specific gravity of the recycle solution, so as to make the extraction by water of the hydrogen peroxide liberated during the oxidation appreciably more complicated.

Likewise, a partial transformation of the alkylanthraquinone to the corresponding alkyltetrahydroanthraquinone is brought about. This latter, which results from the hydrogenation of the aromatic nucleus, is not inert but like alkylanthraquinone possesses a certain capacity for the production of hydrogen peroxide. A number of solutions have been proposed to effect the regeneration of decomposition products of quinone to active quinones, notably treatment by means of oxygen or by another oxidizing agent, in the presence of a mineral or organic base. The major drawback of a process of this type consists in the oxidation of the solvents in the recycle solution.

It has now been discovered that the regeneration of recycle solutions of alkylanthraquinone can be achieved with advantage by treating all or part of the decomposed solution by a hydroxide of an alkali metal in the absence of an oxidizing agent; and optionally, by separating the tetrahydroquinone formed, and by treating it separately by a known method so as to transform it to the corresponding quinone. The treatment of the recycle solution by an alkali metal hydroxide permits a large fraction of the inert decomposition products to be transformed to alkyltetrahydroanthraquinone, without oxidation of the solvents in the recycle solution.

Although the alkyltetrahydroquinone possesses a certain capacity for the production of hydrogen peroxide, it is nevertheless of interest to limit its content in the recycle solution; in fact, since its rate of oxidation is lower than that of the quinone nonhydrogenated at the nucleus, it leads to a reduction in the conversion rate and hence in the production capacity for hydrogen peroxide. Moreover, since its solubility is generally less than that of the corresponding quinone nonhydrogenated at the nucleus, there is the risk that if the concentration becomes too high, it will separate out during the process of manufacturing hydrogen peroxide. It is thus of particular advantage to separate by cooling and subsequent precipitation a large part of the alkyltetrahydroanthraquinone formed during the regeneration treatment, and to treat it separately, for instance by oxidation in an alkaline medium, in order to transform it to the corresponding quinone. This latter can then be recycled in its turn.

The basic reagents which are particularly suitable are caustic soda and potash, in the solid state as well as in solution in water, in alcohol, or in other solvents. Ammonia in the gaseous state gives less good results. The regeneration can be carried out continuously as well as discontinuously. The treatment can be applied to the whole of the recycle solution or only to a part of it. The regeneration is already achieved when the basic reagent is present at the rate of 0.1% on the amount of recycle solution to be treated. In solution, experiments have preferably been carried out at a 5 N concentration, but good regeneration is also obtained with 1 to 10 N NaOH or KOH solutions.

In order to prevent the dissolution of hydroquinones in the aqueous phase, the recycle solution must be treated after completion of the oxidation stage. The treatment is already attained when it is carried out at room temperature. It is of advantage to operate at a higher temperature, optionally at the boiling temperature of the reaction medium. By following the method of the process, oxidation of the solvents for the alkylanthraquinones is avoided. Moreover, the regeneration can be carried out at an elevated temperature without loss of solvent, which proves extremely difficult when treatment is carried out in the presence of an oxidizing agent, air or oxygen for example.

The process is applicable whatever the nature of the alkyl substituents of the anthraquinone and whatever the solvents or solvent mixtures employed. In the following example, the alkylanthraquinone, for example the 2-ethyl, 2-propyl, tert. butyl, amyl, octylanthraquinones, are dissolved in a mixture of approximately equal volumes of an aromatic hydrocarbon and of a secondary alcohol with 9 C-atoms. However, solutions prepared by means of other solvents can be treated in the same manner for the regeneration of decomposed alkylanthraquinones.

Hydrogen peroxide is manufactured with the aid of a recycle solution whose initial alkyl

anthraquinone content is 264 g./kg. After a large number of recycling stages, this solution contains only 156 g. per kg. of active quinones, consisting of 122 g. of alkylanthraquinone and 34 g. of alkyltetrahydroanthraquinone; 100 g. of this solution are treated, while boiling, with 0.1 g. of NaOH cubes for 15 minutes in the absence of air. After separation of the alkali and washing with water acidified with dilute HNO_3, the active quinone content of the solution is 226 g./kg., being 125 g. of alkylanthraquinone and 101 g. of alkyltetrahydroanthraquinone. An amount of alkyltetrahydroanthraquinone corresponding to 38 g./kg. of solution separates from the solution as it is restored to room temperature.

By Contacting with Water-Soluble Base and Oxidizing Agent

Howe, B.K., Andrus, S., and Davies, G.N. (19): Previously, it had been disclosed that the degraded working solution may be regenerated by contacting the working solution with solid catalysts such as activated magnesia or alumina, at a temperature of above 55°C. This regeneration process can be employed at any stage of the cycle, but it is found to be most effective when applied to the solution which has been oxygenated and then extracted to separate the hydrogen peroxide, e.g., to the solution just before it reenters the hydrogenator. Another material found effective in reconverting these so-called degraded autoxidation solutions is sodium aluminum silicate.

It has now been found that reconversion of inert compounds in the working solutions to peroxide-producing substances may be effected by a combined treatment of the degraded solution with an organic or inorganic base and with an oxidizing agent. Enough base should be present to keep the solution basic throughout the oxygen absorption. Preferably the base is a water-soluble base such as an alkali metal hydroxide, in alcoholic solution, and the treatment with the base and oxygen or other oxidizing agent is carried out on a portion of the organic solution withdrawn from the cycle, that portion being washed with water prior to its return to the cycle.

Preferably also, the treatment of the degraded solution is carried out in combination with a treatment of the degraded solution with a bed of particulate solid material, for example, a porous artificial aluminum silicate well known per se for the reconversion of degraded solutions. The bed treatment is effected either before or contemporaneously with the treatment with the base and oxidizing agent; in the latter case, a portion of the cyclic solution is subjected to the treatment with the base and oxidizing agent, while the remainder or a portion of the remainder is contacted with the bed. In the bed treatment, the degraded working solution is preferably contacted with sodium aluminum silicate at a temperature of at least 90°C.

It is unnecessary to raise the temperature of the degraded solution to obtain satisfactory reconversion. When applied to the cycle, the reconversion technique is effected after the oxidized solution has passed through the hydrogen peroxide aqueous extraction column and before this solution enters the hydrogenator. With certain solvents, free base is undesirable in the system; in these circumstances the batch of degraded solution being treated is water washed before return of the treated organic solution to the cycle. Thus, the base should be water-soluble. Since alkalis such as sodium hydroxide attack aluminum it is desirable to use equipment made of stainless steel in those parts of the cycle where, as a result of this treatment, alkali is present.

As will be seen from the results given below, the reconversion obtained is greater normally than that obtained with the solids previously mentioned. In these circumstances, when embodying the process in the cycle it is best to take advantage both of the increased conversion obtained by the process and the rather easier method of operation possible with the solids. Thus, a portion (say 10%) of the cyclic solution is passed continuously through a bed of the particulate solid, while a portion of the remainder (say 10%) is treated batchwise in accordance with the new method. The reaction vessel may be of the kind often used for the oxidation of the reduced solution, i.e., one in which air is bubbled through the solution having entered the reactor through a gas disperser. If desired, an agitator may be fitted.

With solutions containing 40% of unidentified material as subsequently defined, about 1 liter at normal temperature and pressure of O_2 and preferably 3 to 4 l. at normal temperature and pressure of oxygen should be contacted with each liter of degraded solution. Smaller quantities of oxygen may prove effective, though the amount of oxygen required for effective conversion is always greater than that dissolved in the cyclic solution and present at the stage of the cycle in question. In certain circumstances, it may be possible to provide sufficient oxygen in the form of hydrogen peroxide at the stage of the cycle in question by lowering the extraction efficiency. In this case care should be taken lest other than minimal amounts of oxygen and/or hydrogen peroxide find their way to the hydrogenator. It is, of course, possible to treat both solids recovered from the cyclic solution as well as concentrated solution containing the degraded intermediate.

A most advantageous embodiment of this process, which allows for considerable reconversion of degraded anthraquinones, involves the use of sodium hydroxide or potassium hydroxide as the water-soluble base in 8 to 17 Normal aqueous solutions. Such concentrations are particularly advantageous where an ester, for example, methylcyclohexanol acetate, is employed as a solvent for the anthraquinone. It is found that these highly concentrated solutions of sodium hydroxide and potassium hydroxide repress the rate of hydrolysis of the ester solvents, while at the same time give enhanced rates of reconversion of the working solution. In addition, it is found that the rate of reconversion increases with increase in alkali strength of the solution, and that concentrations in excess of 17 Normal tend to cause undesirable side reactions.

Tables 2.3 and 2.4 relate to the treatment of 1:1 solvent mixtures of xylene and methylcyclohexyl acetate containing 2-ethylanthraquinone, tetrahydroethylanthraquinone and their degradation products, referred to as "Unidentified Material". Working solutions comprising other anthraquinones, e.g., methyl-, propyl-, isopropyl-, and butylanthraquinones and other solvents can be regenerated effectively in the same manner regardless of the conditions during the cyclic process, and, in particular, the catalyst used, which in this case was carrier-supported palladium.

The heading "conversion" refers to percentage conversion and is calculated as follows:

$$\text{(a)}\quad \text{Conversion percent} = 100 \times \left[1 - \frac{(\text{Final total solids}) - (\text{Final total quinones})}{(\text{Initial total solids}) - (\text{Initial total quinones})}\right]$$

Equation (a) gives an approximate percent reconversion, because it does not take into account the effect of small variation in total solids concentration which occurs as a result of the treatment. Accordingly, "reconversion" would be more accurately calculated as follows:

$$\text{(b)}\quad \text{Reconversion percent} = 100 \times \left[1 - \frac{\text{Final percent unidentified material in total solids}}{\text{Initial percent unidentified material in total solids}}\right]$$

This equation is only employed in tabulating the results set forth in Table 2.6.

In all the following experiments 50 milliliters of the organic solution, the solids content of which is given in the first line of figures in Table 2.4, were added to a glass shaker vessel of about 150 milliliter capacity which was agitated at the rate of 300 cycles per minute, there being a connection to a calibrated gas burette filled with oxygen. The base was added to the reaction vessel through a side arm and the reactions performed at 21°C.

In Table 2.3 the effect is measured in terms of time for an uptake of 75 milliliters of oxygen to occur, different bases being employed. Comparison of results in Table 2.4 shows that the reconversion obtained with sodium hydroxide and oxygen alone is equal to that obtained first by treatment with particulate sodium aluminum silicate and then with the combined sodium hydroxide/oxygen treatment. "EAQ" means ethylanthraquinone and "H_4EAQ" means tetrahydroethylanthraquinone.

TABLE 2.3: EXPERIMENTAL RESULTS

Base	Quantity	Time to take* up 75 mls. O_2 (minutes)
Aqueous sodium hydroxide:		
4 N	50	4
2 N	50	26
N	50	50
N/10	50	200
Aqueous potassium hydroxide:		
2N	50	12
N	50	39
Alcoholic potassium hydroxide: N/10	15 (EtOH)	>½
Sodium ethoxide:		
N/5	10	>½
N/10	10	1½
Concentrated ammonia	15	140
Saturated calcium hydroxide	50	240
Pyridine	50	85
Triethylamine	50	12
	7.5(+7.5 EtOH)	10
	2(+13 EtOH)	17

*Total uptake approximately 100 milliliters.

In the experiments, the results of which are tabulated in Table 2.5, 50 milliliters of the organic solution described above, the total solids content of which was 100 grams per liter before treatment (of which 32 grams per liter was ethylanthraquinone, 29 grams per liter was tetrahydroethylanthraquinone, and the remainder was "unidentified material") were added to a glass shaker vessel of about 150 milliliters capacity and shaken in an atmosphere of oxygen with the same volume of alkali, or with 0.375 mol of the solid alkali.

TABLE 2.4: EXPERIMENTAL RESULTS

Treatment given to the degraded solution (degraded solution referred to as "O")	Analyses relative to grams/liter for total solids			Conversion (percent)
	Unidentified Material	EAQ +H_4EAQ	Total Solids	
"O" before treatment (i)	40	60	100	----------
"O" treated with 4 N-NaOH/O_2 (ii)	23	77	100	43
"O" treated with Doucil (iii)	32	68	100	20
Solution (iii) treated with 4 N-NaOH/O_2	25	75	100	22

(NOTE.—Indicating further reconversion—the final result being approximately equal to that obtained by treatment of "O" with 4 N-NaOH/O_2 only.)

The first column of Table 2.5 indicates the treatment given, the second column gives the concentration of ethylanthraquinone in grams per liter, the third column the concentration of tetrahydroethylanthraquinone in grams per liter, and the concentration of total solids is given in the fifth column. The concentration of "unidentified material" after treatment is provided by substracting the figures in column 4 from the figures in column 5. The percent reconversion is given in column 6.

TABLE 2.5: EXPERIMENTAL RESULTS

Treatment	EAQ (g./l.)	H_4EAQ (g./l.)	Total (g./l.)	Total Solids (g./l.)	Percent Reconversion
(1)	(2)	(3)	(4)	(5)	(6)
3 N=NaOH	36.0	41.0	77.0	101.6	41.0
3 N=KOH	34.5	43.5	78.0	99.4	43.5
12 N=NaOH	42.0	41.0	83.0	102.1	56.5
12 H=KOH	43.0	39.0	82.0	95.1	54.0
Solid NaOH	47.0	30.5	77.5	98.3	42.5
Solid KOH	48.0	19.0	67.0	87.9	45.0

The oxygen uptake at room temperature and pressure associated with reconversion only was in the region of 100 milliliters. In the experiments with solid sodium and potassium hydroxides, considerable dehydrogenation also took place, accounting for a further 200 to 300 milliliters of oxygen uptake.

Table 2.5 shows that in experiments utilizing low concentrated aqueous solutions of potassium and sodium hydroxides in the range of 3 N, the percent conversion, though of a high order, is not as great as the percent conversion obtainable when the normality of the solution is in excess of 8 N up to 17 N. Table 2.4 also shows that when the concentration of sodium and potassium hydroxide is in excess of 17 Normal, that the percent reconversion is also reduced, though a high order of reconversion is obtainable. Thus, most desirable

results in terms of enhanced percent reconversion is obtainable when the sodium hydroxide and potassium hydroxide are employed in aqueous solution in concentrations described above.

Utilizing the Equation (b) described above for the determination of reconversion and the procedures described for the experiments employed for obtaining the results tabulated in Table 2.5 above, the following results were found and tabulated in Table 2.6.

TABLE 2.6: EXPERIMENTAL RESULTS

Treatment	Initial total solids (g./l.)	Composition of initial total solids		Composition of final total solids		Reconversion (percent)
		Quinones (percent)	Unidentified (percent)	Quinones (percent)	Unidentified (percent)	
3 N-NaOH	100	61	39	75.9	24.1	38
3 N-KOH	100	61	39	78.4	21.6	45
10 N-NaOH	97	60.7	39.3	80.5	19.5	50
12 N-NaOH	100	61	39	81.2	18.8	52
12 N-KOH	100	61	39	86.3	13.7	65
14 N-NaOH	97	58.4	41.6	78.4	21.6	48
17 N-NaOH	97	60.7	39.3	80.1	19.9	49
17.75 N-NaOH	104	62.5	37.5	81.8	18.2	51.5
Solid NaOH	100	61	39	78.9	21.1	46
4 N-NaOH	97	60.7	39.3	73.3	26.7	32
5 N-NaOH	97	60.7	39.3	72.5	27.5	30
6 N-NaOH	97	60.7	39.3	72.1	27.9	29
7 N-NaOH	97	60.7	39.3	71.7	28.3	28
8 N-NaOH	97	60.7	39.3	74.5	25.5	35
10 N-NaOH	97	60.7	39.3	74.5	25.5	35
17 N-NaOH	97	60.7	39.3	72.1	27.9	29

By Thermal Treatment in Inert Atmosphere

Pittsburgh Plate Glass Co.; Baker, P.H., and Cook, J.A. (21): In this process, organic working solutions of quinones such as 2-alkylanthraquinone which have reduced hydrogen peroxide forming capacity, for example because they have through use built up significant quantities of degradation products of the quinones are, after removal of solvent, subjected to elevated temperatures above 200°C., usually at least 250°C. but rarely above 300°C., for limited periods of time in an inert atmosphere. Thus, in a typical method, a working solution which evidences declining capacity to generate hydrogen peroxide is removed from the cyclic system and freed of most if not all of its solvent, leaving a solvent-lean residue which is heated above 200°C. for at least 5 minutes and usually for from 3 to 90 minutes.

An inert atmosphere is provided autogenously by the vapors or residual solvent, but may also be supplied by introducing an inert gas such as nitrogen if desired. This heating procedure causes a significant decline in the "inert solids" (materials which do not generate hydrogen peroxide readily) and corresponding increase in "actives" or hydrogen peroxide generating capacity. Thereafter, the treated residue of organic material having enhanced capacity to generate hydrogen peroxide is returned to the cyclic system, for example, by first dissolving it in carrier solvent and, when necessary, filtering to remove any insoluble material, notably inorganic material such as catalysts which may have been added to enhance the effect of the heat treatment.

It is preferable to withdraw working solution from a point in the cyclic process which is subsequent to the extraction of hydrogen peroxide but prior to hydrogenation, although it may be withdrawn at other points in the cyclic process. Working solution prior to hydrogenation, but after extraction of hydrogen peroxide contains 2-ethyltetrahydroanthraquinone or like tetrahydroquinone in the cyclic system. As the working solution is recycled, the amount of tetrahydroquinone and more highly hydrogenated material increases while the 2-ethylanthraquinone or like quinone concentration decreases correspondingly until the hydrogen peroxide generating capacity of the working solution has decreased significantly and ultimately has become impractically low. This deterioration may be followed by periodic analyses of the working solution.

One convenient method of following the hydrogen peroxide generating capacity of the working solution, which is often employed, comprises hydrogenation of a test portion of the working solution. This hydrogenated test portion of the working solution is then subjected to subsequent oxidation and extraction to generate the equivalent hydrogen peroxide which may be determined analytically without isolation. Thus, it is not necessary to determine the actual composition of the working solution in order to periodically determine its hydrogen peroxide generating capacity. When this technique is employed with a working solution, it is customary to express directly the hydrogen peroxide generating capacity per liter of working solution.

Thus, a working solution which contains 150 grams of 2-ethylanthraquinone per liter of solution has a hydrogen peroxide generating capacity of 21.6 grams of hydrogen peroxide equivalent. At 50% conversion to the reduced or hydroquinone form, the solution is said to carry 10.8 grams of hydrogen peroxide, since this amount of hydrogen peroxide would be released by oxidation of such a working solution. Hence, in the practice of this process, periodic withdrawal for regeneration of a portion of the working solution is made when the direct determination of its hydrogen peroxide forming capacity indicates that such capacity has decreased to 4.0 grams of hydrogen peroxide equivalent per liter of solution or even less, depending upon economics. When it is desired to continuously withdraw the working solution for regeneration, the same method of measuring the hydrogen peroxide forming capacity may be used to determine whether the rate of withdrawal is at a level sufficiently high to provide increased hydrogen peroxide forming capacity.

Vacuum distillation is most frequently employed to remove solvent from depleted working solution. The temperature and pressure employed may vary widely, depending on many factors but are chosen in particular according to the distillation temperature of the specific solvent or solvents. It is also sound practice to use conditions which are not destructive of the solvent so that it may be recovered in useful form. Thus, to distill a depleted working solution comprised of 2-ethylanthraquinone derivatives, methylcyclohexyl acetate and dodecyl benzene, the working solution may be distilled in a conventional apparatus under about 20 millimeters of mercury absolute pressure, while raising the temperature to 150°C. in the distillation residue. At a higher pressure, a higher temperature is required. Any other temperature and pressure combination may be employed, providing the solvent is readily removable without decomposition of the residue.

The residue resulting is substantially, but not necessarily entirely, solvent-free and is suitable for treatment in this process. Up to approximately 15, and quite often above 10,

percent of the residue by weight may be solvent, although lesser or greater amounts of solvent may be contained in the residue. The amount of solvent left in the residue, among other things, depends upon economics, since solvent may deteriorate or otherwise be lost in the regeneration treatment. Usually it is sound practice to remove as much solvent as 90 to 99% or more of all solvent in the working solution prior to treatment.

The temperature at which substantially solvent-free residue is heated ranges upwardly from 200° to 250°C. or somewhat higher, and is maintained until substantial regeneration of actives (or hydrogen peroxide forming compounds) is accomplished. For example, with working solutions in which the active material is 2-ethylanthraquinone, the heating is continued until there is a marked increase in this quinone and/or its tetrahydro derivative, but discontinued before conversion to one or both of these compounds either comes to a halt or the rate of conversion becomes too slow to be justified. Temperatures above 250°C. and as high as 300°C. or higher are possible. Above 275°C. some undesirable decomposition may occur with various alkylanthraquinones.

The heating period may be very short, i.e., as little as several minutes, 5 minutes for example at approximately 300°C. At 250°C., a heating period of 40 to 60 minutes produces the maximum conversion to quinones and minimum of inerts when 2-ethylanthraquinone is the active ingredient. Similar effects are attainable with other like alkylanthraquinones. Unduly extended treatments of 5 or 6 hours usually do not achieve as good a degree of reversion as that which is attained by the shorter treatment periods.

In a perferred embodiment of the process, catalyst is employed to facilitate conversion (reversion) of inerts to actives such as 2-ethylanthraquinone. Illustrative of the type of catalyst preferred are those which provide high surface area, notably sodium alumina silicates. Any inorganic silicon compound providing high surface area such as silica, silica gel, inorganic silicates, viz., calcium silicate, mineral silicates, viz., magnesium silicate and especially mixed silicates, notably those having Na_2O:Al_2O_3:SiO_2 ratios from 1:1:1 up to 1:1:5, may be employed with valuable results. Other materials which have high surface area often may be employed with satisfactory results. Illustrative are bone charcoal, wood charcoal, channel black, precipitated metals such as nickel or palladium, and metal oxides of Groups III, IVB and VB of the Periodic Table of Elements, viz., iron oxide (ferric), alumina, titanium dioxide and vanadium pentoxide. Generally, any material having a surface area of from 5 to 1,000 meters per gram may be employed. The preferred materials of the silicate type have surface area values of from 5 to 400 meters per gram.

In those embodiments of the process which employ catalysts, the catalyst in predetermined amount is added to the substantially solvent-free recovered 2-ethylanthraquinone derivatives obtained by distilling to remove therefrom most of the solvent as subsequently described. The distillation residue mixture with catalyst is heated until the desired conversion results, after which the regenerated solids are dissolved in solvent and filtered to remove catalyst. Use of catalyst is optional, although valuable. Amounts up to 30 grams or even more per 100 grams of distillation residue are illustrative. Larger amounts cause decreased efficiency of heat transfer. Thus, a preferred amount is about 16 grams of sodium aluminasilicate per 100 grams of distillation residue.

The treated residue may be reintroduced into a cyclic process for production of hydrogen

peroxide by dissolving it in the working solution and by decantation, filtration, etc., removing insoluble impurities on catalyst (when present). Catalyst so separated may be reused with or without further processing. Alternatively, the product may be redissolved in fresh solvent (or makeup solvent), filtered, and returned as a solution for mixture with other working solution. It is expedient to reintroduce the redissolved regenerated solids at a point in the cyclic process after extraction but before hydrogenation. However, such material may be returned to the system at any other point in the cyclic process.

It is usually not desirable to remove the reduced working solution from the cyclic process prior to oxidation for the purpose of redissolving regenerated solids, because of the danger of losing hydrogen gas or because of the possibility of premature oxidation of working solution to form hydrogen peroxide. However, fresh makeup working solution or solvent may be employed to dissolve regenerated solids which may then be reintroduced to the cyclic system at any point including the hydrogenation state. The reclaimed solvent may be employed as makeup solvent for new 2-ethylanthraquinone or as solvent for the regenerated 2-ethylanthraquinone derivatives. If desired, solution of the product may also be prepared in solvent other than the initial or recovered solvent mixture.

The process has been described particularly in terms of a principal embodiment employing 2-ethylanthraquinone and its derivatives, but it is also applicable to quinones and especially other alkylanthraquinones, such as 2-n-propylanthraquinone, 2-isopropylanthraquinone, 2-n-butylanthraquinone, 2-sec-butylanthraquinone, 2-t-butylanthraquinone, 2-t-amylanthraquinone, 2-decylanthraquinone, and their hydrogenated derivatives, or generally any saturated short chain aliphatically monosubstituted anthraquinone which is substituted in the beta position by such an alkyl group containing up to 10 carbon atoms. The following example illustrates the manner in which the process may be performed.

Working solution from storage after water extraction of the hydrogen peroxide content which had become depleted to the extent that its hydrogen peroxide equivalent was approximately 4.0 grams per liter of working solution, was distilled at an absolute pressure of 18 millimeters of mercury until the residue reached a temperature of 150°C. From one liter of such solution there was obtained a residue of 151 grams containing 2-ethylanthraquinone derivatives. This residue was heated to 250°C. with 25 grams of a finely divided sodium alumina silicate (Na_2O:Al_2O_3:SiO_2 percent by weight: 13.98, 19.47, 58.01; 76% coarser than 200 mesh but finer than 100 mesh). Samples of the heated mixtures were withdrawn at intervals and analyzed for 2-ethylanthraquinone, 2-ethyltetrahydroanthraquinone and inert material. Since approximately 15% by weight solvent remained in the initially heated material, all samples were analyzed, for total solids, to permit expressing the analytical results on a solvent-free basis. The following data were obtained.

Heating Time, minutes	EAQ, percent [1,2]	H_4EAQ percent [1,2]	Inert, percent	Useful Quinones, percent
0	27.9	31.6	39.3	60.7
30	44.4	25.6	30.0	70.1
60	45.8	25.6	28.6	70.4
150	44.1	20.8	35.2	64.9
330	47.1	12.5	39.2	59.6

[1] EAQ=2-ethylanthraquinone.
H_4EAQ=2-ethyltetrahydroanthraquinone.
[2] All quantities expressed as percent by weight (solvent-free basis).

Thus, it is shown that 2-ethylanthraquinone increases, while 2-ethyltetrahydroanthraquinone and inert material decrease. In the beginning, the 2-ethylanthraquinone increases by an amount greater than the decrease in 2-ethyltetrahydroanthraquinone, indicating the net result is to form 2-ethylanthraquinone at the expense of the inert material and the total useful quinone content increased. As the treatment proceeds, 2-ethylanthraquinone continues to form.

Addition of Alkaline Material to Working Solution Prevents Degradation of Working Material

Du Pont; Reilly, V.J. (20): It is an object of this process to provide a simple yet effective way of reducing substantially the rate of loss of working material in the operation of an anthraquinone process for producing hydrogen peroxide. This object is accomplished by carrying out the hydrogenation step in the presence of a catalyst-free, solid particulate inorganic alkaline material, which is insoluble in the working solvent of the cyclic process and is in admixture with the solid particulate hydrogenation catalyst employed in the hydrogenation step. It now has been found that the presence of such alkaline material in admixture with the hydrogenation catalyst results in a substantial decrease in the amount of inert degradation products formed, and, therefore, also a decrease in the amount of such degradation products that must be removed from and replaced in the working solution.

Alkaline materials which are effective in this connection are the carbonates of the alkaline earth metals, magnesium and the alkali metals; the bicarbonates of the alkali metals; the hydroxides and oxides of magnesium and those of the alkaline earth metals which are essentially insoluble in the working solution. Specific examples of suitable alkaline materials are sodium carbonate and bicarbonate, calcium and magnesium carbonates and magnesium hydroxide. Others that can be used are strontium and barium carbonates and magnesium oxide. The mineral carbonates such as calcite (calcium carbonate) and particularly marble are preferred, because of their high effectiveness, their ready availability and the physical strength of their particles; furthermore, spent catalyst in admixture with carbonate can be regenerated by air roasting without destroying the effectiveness of either. Another preferred alkaline material is sodium carbonate monohydrate. When this material is used, it can be readily separated from spent catalyst by leaching with water, before subjecting the catalyst to regeneration treatment.

Acidic impurities are normally formed in small but significant amounts in the working solution during operation of the cyclic process. Such impurities appear to promote the undesired side reactions which produce the inert degradation products. The mechanism by which the above alkaline materials function to reduce or inhibit formation of degradation products is not entirely understood, but it is thought that they serve primarily to neutralize the acidic impurities as they are formed. The amount of the particulate, insoluble, catalyst-free alkaline material which should be present in the working solution during hydrogenation is not critical, so long as sufficient is present to neutralize any acidity which may tend to develop. Amounts as small as 0.3%, based upon the weight of the working solution, are effective, but from 1 to 5% will most generally be used and are preferred. Much larger amounts can be used if desired.

The alkaline material employed should preferably be of a particle size similar to that of the

particulate hydrogenation catalyst with which it is admixed. Thus, where the hydrogenation catalyst is employed as particles suspended or fluidized in the working solution by agitation of the slurry, the alkaline material preferably will also be of a particle size that will be readily suspended along with the catalyst in the working solution. When the catalyst is employed in the form of a fixed bed of granules through which the working solution and hydrogen are passed, the particles of alkaline material admixed in the bed with the catalyst are preferably of about the same size as the catalyst particles. In fixed bed operation, particle sizes of the catalyst and of the alkaline material generally will range from about 4 to 100 mesh; whereas in fluidized or slurry operations, the corresponding particle sizes will generally range from 60 to 400 mesh (U.S. Standard Screen Scale).

It has been proposed heretofore to employ hydrogenation catalysts consisting of a noble metal on an alkaline earth metal carbonate (Canadian Patent 600,851), or a magnesium oxide or hydroxide (U.S. Patent 2,930,803) support or carrier. However, such carbonate, oxide or hydroxide catalyst supports have low resistance to attack by the working solution, since the acidic substances which normally develop in the working solution tend to dissolve the catalyst support during use; and precipitated supports such as magnesium hydroxide break up readily when fluidized in the working solution. Furthermore, effective palladium-on-calcium carbonate catalysts are difficult to prepare; when conventional impregnation procedures are employed, most of the palladium is precipitated out as unsupported palladium black (undesirable), while the resulting support with its meager palladium deposit is of relatively low catalytic activity. The process is illustrated by the following example in which all percentages are by weight.

A working solution containing 9.3% 2-tertiary-butylanthraquinone and 7% tetrahydro-2-tertiary-butylanthraquinone in a working solvent consisting of a mixture of methylnaphthalenes and diisobutylcarbinol was employed in a cyclic operation, in which it was subjected repeatedly to successive hydrogenation and oxygenation treatments. Hydrogenation was effected in each cycle at about 45°C. with hydrogen at a pressure of about 1 atmosphere in the presence of about 7%, based upon the weight of the working solution, of a suspended catalyst consisting of 0.6% metallic palladium on activated alumina of a particle size ranging from about 60 to 400 mesh. From about 50 to 55% of the active anthraquinone compounds present was hydrogenated. The hydrogenated working solution thus formed in each cycle was filtered to remove the catalyst, then oxygenated by contacting it with oxygen at about 45°C. and 1 atmosphere pressure. After removing the hydrogen peroxide formed from the oxidized working solution by countercurrent extraction with water, the oxidized working solution was recycled to the hydrogenator.

After 250 hydrogenation-oxygenation cycles, the amount of working material which had become degraded to inert materials, i.e., materials having no H_2O_2-synthesizing value in the process, amounted to 0.17 g. per gram mol of H_2O_2 produced. A total of 315 gram mols of H_2O_2 was produced.

HYDROGENATION STAGE: CATALYSTS

The working solution, which comprises a solvent or a mixture of solvents capable of dissolving the quinone form as well as the hydroquinone form of the working material,

represents a considerable capital investment. As presently processed, the working material may undergo degradation of very significant proportions. This will result in loss of productive working material, with a concomitant loss of hydrogen peroxide production. Such loss may under some conditions be as high as about 13% of workable quinone material in about 2,000 hours of operation.

The commercial operation of the anthraquinone process comprises suspension of the hydrogenation catalyst in the working solution, while the latter is in contact with hydrogen gas. Such an operation is generally referred to as "fluidized" and requires that the average particle size of the catalyst is small; under such circumstances reactivity of the catalyst is high. The catalysts most generally employed as fluidized catalyst are Raney nickel and a catalyst composed of a carrier of activated adsorbent material (such as activated microporous or gamma alumina, or microporous activated silica gel) upon which metallic palladium is deposited.

In the small particulate form in which these catalysts are employed as fluidized catalysts, several hydrogenation reactions proceed simultaneously but with different reaction rates. The predominant hydrogenation reaction is the change of the quinone group to the hydroquinone group or the change of a quinone to a quinhydrone. Proceeding simultaneously with the predominant reaction, nuclear hydrogenation of the anthraquinone tends to occur at a determinable and measurable rate with the formation of tetrahydro derivatives of the working material, but without destruction of the quinone group or the ability alternately to reduce and oxidize that group with the production of hydrogen peroxide.

Other hydrogenation reactions occur simultaneously but at rates below that of hydrogenation of the nucleus. These hydrogenations are also undesirable, since they result in degradation products not capable of being further reduced and subsequently oxidized leading to the production of hydrogen peroxide.

Palladium Deposited on Pretreated Siliceous Carrier Makes an Excellent Hydrogenation Catalyst

Laporte Chemicals Ltd.; Le Feuvre, C.W., and Morgan, C.A. (22): Various catalysts have been proposed for use in the reduction stage, one of the most usual being activated nickel.

U.K. Patent 508,081 mentions the use of active palladium as a hydrogenation catalyst in the reduction of anthraquinones to anthraquinols, but this specification does not disclose how the catalyst was prepared or used. U.K. Patent 686,574 describes a process for the production of hydrogen peroxide in which an alkylated anthraquinone is hydrogenated in solution by means of hydrogen in the presence of a catalyst consisting of metallic palladium supported on activated alumina, the catalyst preferably containing 0.01% to 10% by weight of palladium and being suspended in the solution of the alkylated anthraquinone by means of a stream of hydrogen-containing gas. This specification also discloses the use of palladium catalyst on carriers of silica-alumina, coconut charcoal, active coal carbon, activated lignin carbon, decolorizing vegetable carbon, granular corundum, silica gel, barium sulfate and fibrous asbestos. According to this specification, none of these carriers gives as good results as activated alumina.

It has now been found that satisfactory results in the hydrogenation of alkylated or arylated anthraquinones to alkylated or arylated anthraquinhydrones or alkylated or arylated anthraquinols, can be obtained by using as a catalyst palladium deposited on a siliceous carrier which has been treated with an aqueous solution of an alkali.

Preferably the siliceous carrier is silica gel but other siliceous carriers may be used, such as zeolites including artificial sodium aluminum silicates and silica-alumina catalysts which are water-insoluble silicates or mixtures containing silica. The term "silica gel" as used here refers to a gelatinous activated form of silica. In order to prepare the carrier for making the catalyst, the siliceous carrier, e.g., commercial silica gel, is treated with an aqueous solution of an alkali. Preferably this alkali is sodium carbonate, bicarbonate or sodium hydroxide.

U.K. Patent 580,897 describes a process for the preparation of supported platinum group metal catalysts, in which a silica gel is boiled in a solution containing sodium bicarbonate with or without a wetting agent, this treated silica gel being afterwards washed and palladized in a sodium-palladium-chloride solution. It is claimed that the sodium bicarbonate not only facilitates the hydrolysis of the palladium compound, but also fills the pores of the silica gel, so that the palladium oxide precipitate is concentrated on the outer surface of the gel where maximum concentration of the metal is desirable for this type of catalytic reaction in the liquid phase. The sodium bicarbonate is removed by washing the catalyst prior or subsequent to the reduction of the palladium oxide.

As stated above, the use of silica gel as a carrier for palladium catalyst for use in the reduction of anthraquinones to anthraquinols has already been disclosed in U.K. Patent 686,574. The silica gel used here was, however, not treated with a solution of an alkali and the resulting palladium catalyst was found to be relatively inactive. In the preparation of the palladium catalyst the siliceous carrier, for example silica gel, after treatment with a solution of an alkali, preferably sodium carbonate, is washed twice by decantation and then palladized with a suitable palladium compound, the preferred form being sodium chlorpalladite. The palladized support is then washed and dried and the palladium reduced to the metallic form.

It is preferable for the palladium catalyst material to have a particle size corresponding to a screen aperture between 0.001" and 0.1" and to be suspended in the solution. The use of particle sizes corresponding to a screen aperture finer than 0.001" is undesirable because the catalyst then becomes difficult to filter from the solution, while catalyst particles corresponding to a screen aperture coarser than 0.1" are difficult to suspend in the solution. By using a catalyst of the above particle size it is possible to keep the catalyst in free suspension in solution without agitation other than that provided by the gas stream, thus lengthening the active life and reducing the danger of abrasion and disintegration.

The process is, of course, not restricted to the use of palladium catalyst material having a particle size corresponding to a screen aperture between 0.001" and 0.1", as it is also possible to use the catalyst material in a coarser form which can, for example, be in a fixed bed through which the working solution and the hydrogen gas are passed, either in cocurrent or countercurrent. The palladium catalysts employed according to this process are suitable for use in free suspension in a hydrogenator and, as previously stated, the

catalysts are of such particle size that separation from the solution may be simply achieved by means of filtration or a short period of settling. As previously stated, the catalysts may also be of larger particle size so that they may be used in the form of a fixed bed. The following example illustrates the process and its advantages.

One part by weight of commercial silica gel (100-240 mesh B.S.S.) was boiled for about 5 minutes with 0.2 part by weight of sodium carbonate dissolved in 3 parts by weight of water. It was then washed by decantation with two lots of 10 parts by weight of cold distilled water, the fine dust being thereby removed. The treated silica gel was then sucked dry at a vacuum pump and was afterwards heated to about 100°C. It was subsequently slurried for 5 minutes with 1.5 parts by weight of boiling sodium chlorpalladite solution (containing 13 g./l. of Pd). The palladized silica gel was then washed until neutral, with cold distilled water, sucked dry and dried in an oven at 120°C. The palladium was reduced to the metallic state with hydrogen before use.

The catalyst (2% Pd) was suspended in a hydrogenator vessel in a solution containing 100 g./l. of 2-ethylanthraquinone in a solvent mixture containing equal volumes of benzene and methyl cyclohexanol acetate, the catalyst concentration being 10 g./l. The rate of formation of 2-ethylanthraquinol was 2.8 g. per g. of catalyst per hour, expressed as the equivalent rate of formation of hydrogen peroxide.

Preparation of Hydrogenation Catalyst Consisting of Nickel Based on Inert Support of Porous Cement Type

Societe d'Electrochimie, d'Electrometallurgie et des Acieries Electriques d'Ugine and l'Air Liquide; Sancelme, A. (23): This process is characterized in that the inert support is of the so-called "porous cement" type. As the catalyst will have to undergo thermal treatments during its activation and its possible regeneration, a refractory cement will be used, preferably, for instance an aluminous cement of high purity. All methods suitable for causing the formation of cells in a cement may, a priori, be used, particularly the formation of an emulsion of air bubbles by a vigorous kneading of the paste and the addition of substances capable of being decomposed while evolving gas bubbles before the complete setting of the cement.

Among these substances, carbonates or bicarbonates, hydrazine and various peroxides, particularly hydrogen peroxide, may be mentioned as examples. The latter substance, in particular, gives very good results; it makes it possible to give the desired porosity to the cement, when cold, without introducing substances detrimental to the catalyst or to the strength of the cement. The cement, intimately mixed and crushed, if necessary, with the compound of the active metal, is mixed with the amount of water necessary for obtaining a smooth and consistent paste. A tensio-active element is then added for holding the gas bubbles released during the hardening of the cement.

It is preferable to avoid synthetic agents containing sulfur in their molecules. Excellent results are obtained with a 5% solution of very pure soap in an amount equal to about 2 to 5% of the amount of water used for the mixing. Next, amounts of hydrogen peroxide are added according to the desired porosity (of the order of 1% of the amount of mixing water expressed in amounts of commercial hydrogen peroxide at 35% in weight).

The mixture is then rapidly stirred and poured into moulds. It is left standing as long as possible and it swells under the action of the bubbles of oxygen caused by the decomposition of the hydrogen peroxide in contact with a decomposition catalyst which may be the metal compound itself.

This decomposition is completed, in general, after 45 minutes and often after 15 to 20 minutes, and, in consequence, one will have to operate rapidly so as not to destroy the bubbles and damage the uniform porosity of the cement. The moulds should not be filled so as to leave to the cement the space necessary for its swelling, and the thickness of the blocks should not exceed 15 cm., otherwise the bubbles would have unequal dimensions at the bases and at the surfaces of the blocks.

The temperature plays a predominating part in the rate of decomposition of the hydrogen peroxide; it is necessary, therefore, to always prepare the catalyst at the same temperature, 15° to 20°C. for instance, or even less, if large masses are treated which heat up during hardening or if the metal compounds used are powerful decomposition catalysts for the hydrogen peroxide. The catalyst may be activated by reduction by hydrogen or a gas rich in hydrogen inside the very apparatus in which it is to be used. For catalysts having a nickel base, the reduction takes place between 250° and 600°C., but it has been found that the optimum temperature was between 400° and 500°C. This temperature should be reached gradually and held for 2 to 4 hours. First water vapor is released, then the volatile products of decomposition of the metal salt. The cooling also should be very gradual and should be carried out under a stream of hydrogen.

It is preferable to maintain a suitable ratio between the weight of the metal compound and the weight of cement, generally somewhat less than 1, and a porosity corresponding to an apparent density of 0.8 to 1.1 before reduction. Thus a very appreciable mechanical strength is obtained, which increases, in general, after reduction. The reduction is accompanied only by a slight shrinking (4 to 5%) as compared with that of similar catalysts in wafer form (16 to 20%). This is due to the cement armature which is not very deformable.

It was stated above that the depth imperviousness of these catalysts with a large effective area gave them a long life. Anyhow, when their activity has decreased to a large extent, it is very easy to regenerate them, for instance, by a process comprising the following stages:

(a) Extraction by means of a suitable solvent (methanol for example) of the absorbed organic products.
(b) Possibly an oxidizing roasting for eliminating the nonvolatile impurities, followed by a scavenging by means of an inert gas.
(c) A reactivation by hydrogen in the same conditions as the initial activation, i.e., preferably between 400° and 500°C.

Several successive regenerations may be effected with no substantial decrease in activity being found for these catalysts.

Comparative measurements have been effected between conventional catalysts (Raney nickel, nickel based wafered catalyst, palladium on carbon, palladium on activated alumina, etc.)

and catalysts on aerated cement. All are in favor of the latter type of catalyst, both as regards the duration of activity and from an economic point of view if the price of the catalyst used is referred to the unit of hydrogen peroxide produced.

Activity comparisons have also been effected between catalysts with variable porosities prepared in accordance with the same method, in which only the amounts of hydrogen peroxide involved during the mixing of the cement were different. In the range in which these catalysts offer an interest (specific gravity previous to reduction from 0.7 to 1.3) it may be assumed, as a first approximation, that for a given weight of catalyst the activity is in inverse proportion to the density of the catalyst used. In limiting cases, where the cement is subjected to no treatment intended to make it porous, measurements showed that for a given weight of metal these catalysts with a specific gravity higher than 2 are from 6 to 10 times less active than the corresponding porous catalysts with a specific gravity of about 0.9. Their drop in activity in time and with the successive treatments, further, is much more marked.

The catalysts, according to this process, may be put in action either in the shape of grains or lumps constituting a fixed bed, or in the shape of a powder or fine grains in suspension in a liquid medium. The grains or the powder are preferably graded by sieving. An example is given, subsequently, for the working of the process, in which the metal of the catalyst is nickel, the alkylanthraquinone is the 2-ethylanthraquinone and the solvent for the anthraquinone is heptyl acetate.

A catalyst is prepared according to the following method: 60 g. of nickel oxide, NiO, are mixed intimately with 100 g. of refractory, very pure aluminous cement. After sifting, grinding and mixing, the resulting powder is mixed with 73 $cm.^3$ of distilled water, 3 $cm.^3$ of a 5% soap solution and 1.15 $cm.^3$ of 30% hydrogen peroxide. The cement is poured into a mould where it swells slowly owing to the decomposition of the hydrogen peroxide, until it reaches a volume of 220 $cm.^3$. After a complete hardening under water and drying, this catalyst which has a good mechanical strength, is crushed into grains of 0.3 to 0.5 $cm.^3$. 100 $cm.^3$ of these grains, i.e., 43.1 g. of catalyst, containing 9.85 g. of nickel are reduced at 460°C. in a stream of pure hydrogen. A shrinking of 6% is noted.

After cooling, this catalyst is impregnated with a 9% solution of ethyl-2-anthraquinone in heptyl acetate. Under these conditions, it can absorb 7 $cm.^3$ of hydrogen per minute, owing to the formation of ethyl-2-anthraquinhydrone, which can be oxidized later into ethyl-2-anthraquinone and hydrogen peroxide. It will be noted that 100 $cm.^3$ of a similar catalyst in grains, not having undergone the treatment for making it porous and containing 16.2 g. of nickel, treated in quite a similar manner, allow the absorption of 1.3 $cm.^3$ only, per minute, with the same solution.

Reactivation of Reduction Catalyst in situ by Treatment with Inert Gas

Pittsburgh Plate Glass Co.; Hungerford, F.H., and Samelson, R.J. (24): In the practice of the anthraquinone process, the catalyst gradually loses its activity and must be replaced or further catalyst added. Where the life of the catalyst is short, the catalyst cost can become excessively high and constitute an unreasonable portion of the cost of producing hydrogen peroxide.

Normally, catalyst of reduced activity or spent catalyst is withdrawn from the system and subjected to special treatment for reactivation. Prior to this process, no method of reactivating the catalyst in situ appears to have been provided.

A simple method of reactivating the catalyst has now been provided, which is especially advantageous since it can be performed without removal of the catalyst from the solution or suspension of anthraquinone and/or anthraquinol. Thus, the catalyst activity may be improved in situ in the hydrogenation zone, or a portion of the catalyst suspension in the quinone may be withdrawn from the hydrogenator and reactivated. It has been found that this may be accomplished by periodically decreasing the pressure of elemental hydrogen in contact with the catalyst and the quinone and/or quinol solution undergoing hydrogenation, and subsequently passing a gas which is inert to the quinone and quinol into the suspension containing the catalyst while the hydrogen pressure has been so reduced. After the catalyst has been reactivated, or at least after its activity has been substantially increased, the hydrogen pressure in the hydrogenator is increased, usually to its initial level, and hydrogenation is continued.

In accordance with one simple embodiment of the process, hydrogen is passed through a solution of the alkylanthraquinone in which a catalyst is suspended. After the process has been conducted long enough so that the activity of the catalyst begins to diminish, introduction of hydrogen into the solution is discontinued; subsequently, an inert gas, such as nitrogen, is passed through the catalyst-quinol suspension for a suitable period of time. This inert gas contains little or no hydrogen, although a certain amount of residual hydrogen normally is present in the system for a substantial period after hydrogen introduction is discontinued. In any event, the hydrogen pressure in the hydrogenator is substantially less (usually at least 0.1 to 0.3 atmosphere less) than that established during regular hydrogenation. Alternatively, the process may be conducted reactivating the catalyst using an inert gas which contains some hydrogen but in which the hydrogen partial pressure is below (usually at least 0.1 to 0.3 atmosphere below) that at which the hydrogenation normally is conducted.

An effective method of conducting the hydrogenation at a relatively rapid rate is to introduce the hydrogen into the quinone solution more rapidly than it is absorbed and recycling the unabsorbed hydrogen together with makeup. Thus, gaseous hydrogen may be introduced into the lower portion of a pool of quinone solution containing catalyst and the unabsorbed hydrogen allowed to escape from the surface of the liquid. This unabsorbed gas is then mixed with enough fresh hydrogen to make up for that absorbed, and the resulting mixture is recycled to the lower portion of the pool.

In the practice of this recycle operation, catalyst is reactivated periodically by discontinuing the addition of fresh hydrogen and instead introducing inert gas into the recycling hydrogenating gas. As cycling proceeds, hydrogen continues to be absorbed, the hydrogen partial pressure in the gas entering the pool falls, and the inert gas partial pressure rises. This continues until the catalyst activity has been largely restored or at least substantially increased. Subsequently, introduction of inert gas is discontinued or its rate of introduction is decreased and hydrogen is introduced into the recycling gas stream, thus raising the partial pressure of the hydrogen in the gas entering the pool to substantially its initial level.

The treatment of the catalyst suspension with inert gas may be effected at any convenient temperature below that at which substantial decomposition of the solution or quinol takes place. Temperatures of 50° to 150°F. are suitable. However, higher temperatures may be used. The time during which the inert gas is introduced as described normally ranges from 20 minutes to 4 hours; longer periods may be used, if desired.

In accordance with a further embodiment of the process, a slurry of catalyst in solution or suspension of anthraquinone may be withdrawn continuously or periodically from the hydrogenator and the catalyst reactivated by passage of inert gas through the slurry. This frequently is advantageous since it affords a convenient method for reactivating the catalyst without shutting down the hydrogenator. Thus, hydrogenation of anthraquinone may be continued without interruption in such a case and the withdrawn slurry, after treatment with nitrogen or like inert gas, may be returned to the hydrogenator. Any convenient gas which is inert with respect to the solvent, the quinone, and the quinol, may be used for the purpose including nitrogen, argon, carbon dioxide, helium, methane, ammonia, or the like. The following is a typical example.

The system used for production of hydrogen peroxide involved a hydrogenator vessel with a capacity of 150 gallons, an oxidizing vessel with a capacity of 150 gallons, and an extraction column, all connected together. The solution used was a mixture of 2-ethylanthraquinone and 2-ethyltetrahydroquinone dissolved in alkyl benzenes with a boiling range of 365° to 415°F. and predominantly consisting of alkyl benzenes containing 10 to 11 carbon atoms. This solution contained about 30 grams per liter of 2-ethylanthraquinone and 30 grams per liter of 2-ethyltetrahydroquinone.

The system was charged with this solution, about 100 gallons being in the hydrogenator and 150 gallons in the oxidizer. Circulation of solution was commenced at the rate of 5 gallons per minute, solution being withdrawn from the hydrogenator through a filter to remove catalyst, and the filtered solution was delivered to the oxidizer. The solution from the oxidizer was delivered to the bottom of a continuous extractor, water being supplied to the top of the column, and the extracted solution was transferred from the top of the column to the hydrogenator.

After circulation was commenced, the hydrogenator was purged with nitrogen, and 3 pounds of metallic palladium catalyst on aluminum silicate carrier was suspended in the solution in the hydrogenator, and hydrogen gas was introduced into the lower portion of the hydrogenator at a rate such as to hold the catalyst in suspension. Unabsorbed hydrogen rose through the pool and was collected outside the hydrogenator, a portion purged, and the remainder recycled to the bottom of the hydrogenator, additional hydrogen being added continuously. The amount of such hydrogen recycled was 550 cubic feet per hour. The amount of additional hydrogen introduced was 200 cubic feet per hour and the amount of purge 50 cubic feet per hour, all measured at 760 millimeters pressure and 70°F.

The process was continued over a period of many days, the amount of catalyst in the hydrogenator being initially sufficient to establish the quinol content of the solution, leaving the hydrogenator equivalent to 6.97 grams of H_2O_2 per liter. As time went by, further catalyst was added to hold the quinol content above about 5 grams per liter H_2O_2. However, this quinol content gradually decreased to an equivalent of 4.06 grams of H_2O_2 per

liter. Consequently, the introduction of hydrogen into the recycle system was stopped, circulation of solution being continued. Nitrogen was introduced into the solution in the hydrogenator at the bottom of the pool of this solution at a rate of 100 cubic feet per minute measured at 70°F. and one atmosphere absolute pressure, the gas escaping from the top of the hydrogenator being recycled and a purge of 50 cubic feet per hour being taken as before. Nitrogen introduction was continued at this rate for 4 hours while the solution was at a temperature of 115°F.

During this period, hydrogen was purged from the system and, within an hour, the amount of hydrogen was below 20% by volume of the gas flowing through the hydrogenator. After 4 hours, nitrogen introduction was discontinued and hydrogen introduced at the rate specified above. The degree of hydrogenation which then took place was equivalent to 5.42 grams of H_2O_2 per liter of solution, no catalyst being added or removed.

Fixed Bed Hydrogenation Catalyst Increases H_2O_2 Yield and Reduces Degradation of Working Material

FMC; Porter, D.H. (25): The hydrogenation of the quinone form of the working material presents particular problems because of the fact that during the hydrogenation stage, concurrent and undesired reduction reactions proceed with the main reduction, the latter being reduction of the quinone group to the hydroquinone group. The hydrogenation of the working material is effected in the presence of a hydrogenation catalyst, such as Raney nickel or a noble metal supported upon an inert carrier, and the wanted reduction reaction, by reason of ancillary activity of the catalyst in inducing other hydrogenation reactions, is less than theoretical.

Such ancillary reducing reactions may produce nuclear hydrogenation of the aromatic nucleus of the working material with the production of a tetrahydro derivative thereof. There may also be produced unwanted and undesirable nonusable by-products, that is, by-products in which the capacity of the quinone group to be alternately reduced and oxidized has been lost. All of these undesirable reduction reactions, it is believed, proceed at a slower rate than the wanted reduction reaction and appear probably to be due to excessive time of contact with the hydrogenation catalyst. It is an object of this process to provide a hydrogenation procedure in which contact between the working material and the catalyst in the presence of hydrogen is reduced to a minimum.

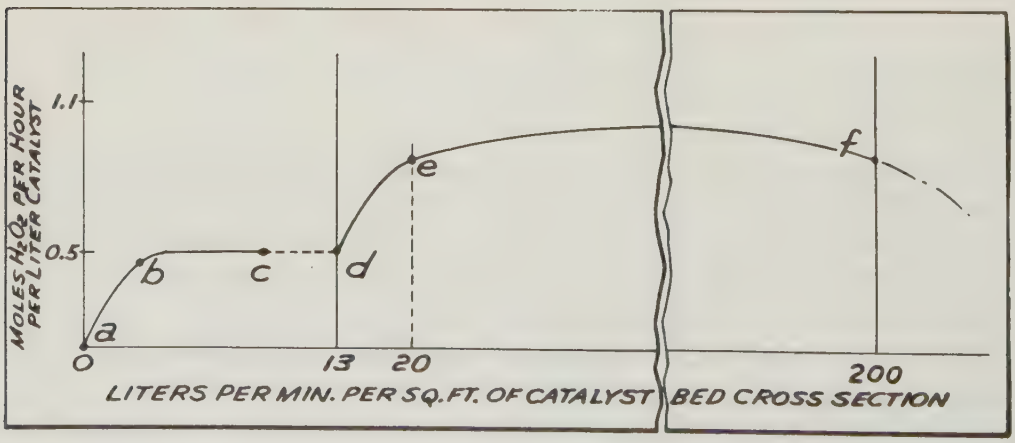
As catalyst, the process employs any suitable catalyst known to foster the reduction of the quinone group to the hydroquinone group, as for instance Raney nickel or one of the noble metals ruthenium, rubidium, platinum, rhodium or palladium. Palladium being one of the commercially better known catalysts for use in the anthraquinone process is illustrated here as the catalyst employed, and when so employed is present upon a catalyst carrier and in a fixed bed in contrast to the commercial utilization of hydrogenation catalysts in very finely divided form suspended in the working solution, all as exemplified in Hinegardner U.S. Patent 2,689,169, and in Sprauer U.S. Patent 2,657,980. In order to effect that the catalyst and working solution have a relatively short time of contact in the presence of hydrogen, the catalyst, that is the carrier and supported metal, is selected as to average particle size to a close tolerance with a mesh size of from about 4 mesh to about 100 mesh. The working solution should be passed rapidly over and through such a catalyst bed at a

very high rate of feed, preferably between 20 liters to 200 liters per minute per square foot of catalyst bed cross-sectional area. The temperature of hydrogenation may be the conventional temperature employed, namely, from about room temperature to about 100°C., although it is suggested that the temperature be maintained in the lower ranges.

In order to effect hydrogenation, hydrogen gas may be dissolved in the working solution or admitted to the hydrogenator so long as contact be obtained between the hydrogen gas and the working solution in contact with the catalyst and, in this mode of operation, the catalyst will be surrounded by working solution. As is known in the art, the hydrogen pressure may vary from somewhat below atmospheric to approximately 25 atmospheres. The procedures specifically described here are applicable to general hydrogenation of the alkylated anthraquinones using metal or the noble metal catalysts, such as ruthenium, rubidium, platinum, rhodium, palladium, upon a support, so that a fixed bed can be prepared thereon containing catalyst particles of 4 to 100 mesh size. Such supports may be carbon, the carbonates of the alkaline earth metals, such as magnesium carbonate, calcium carbonate, strontium carbonate and barium carbonate, the carbides such as magnesium carbide, silicon carbide, aluminum carbide, titanium carbide and zirconium carbide, and the oxides of magnesium, silicon, aluminum, titanium and zirconium.

In a series of experiments, a given working solution of a stated composition of working material and working solvent was passed in contact with hydrogen gas, at constant pressure, through a fixed bed of palladium catalyst; and it was determined that a relatively constant amount of the hydroquinone form of the working material could be produced at moderate flow rates of the solution and hydrogen over the catalyst. This is shown at a-b-c in the curve of Figure 2.4a.

FIGURE 2.4a: HYDROGEN PEROXIDE PRODUCTION PLOTTED AGAINST FLOW OF THE WORKING SOLUTION THROUGH THE BED



Source: D.H. Porter, U.S. Patent 3,009,782, November 21, 1961

However, when the flow rate exceeded about 13 liters per minute per square foot of catalyst area, the amount of hydroquinone produced increased relatively rapidly until a constant and maximum was reached at a flow rate of 20 liters per minute. The amount of hydroquinone produced remained substantially at this constant and maximum level for flow rates up to about 200 liters per minute per square foot of catalyst area. The data represented by Figure 2.4a on the line a-b-c-d corresponds to production heretofore known to be available from the prior art. Thus, on increasing the velocity rate, as shown by the curve on the portions a-b, it was known that an increase in hydrogen peroxide was obtainable until a relatively constant figure was obtained as is shown in portion of curve b-c.

However, in this process, the flow rate was increased beyond rates so far considered, and, from a flow rate of about 13 liters per minute per square foot of catalyst bed area, the yield of peroxide was increased rapidly with increasing flow rate, up to a flow rate of about 20 liters per minute per square foot of bed cross-section. At the 20 liters per minute per square foot rate, the yield of peroxide reached is at a relatively constant and maximum level such that at flow rates of between 20 to 200 liters per minute per square foot of cross-section of catalyst bed, the yield of peroxide remains at a high level. This is because the increased flow rate induces an increase in concentration of hydroquinone form and therefore, in direct proportion, an increase in hydrogen peroxide yield as shown on the curve d-e-f.

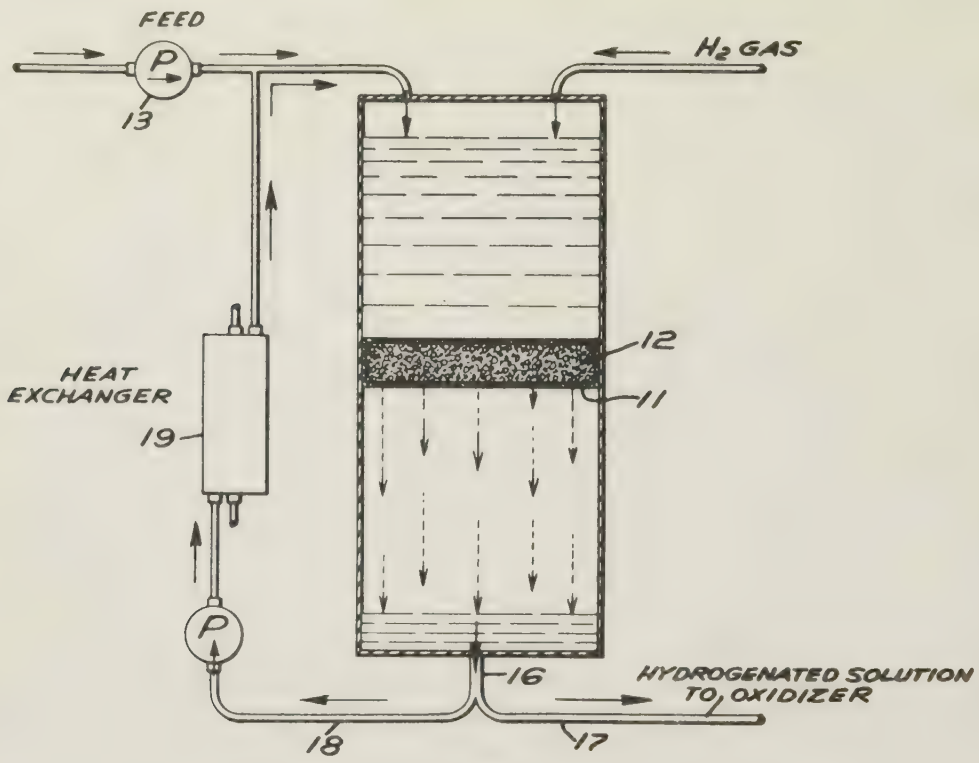
Referring to Figure 2.4b, a hydrogenator column is shown generally at 10 which is equipped with a fixed bed 11 filled with granular catalyst 12 of the type above described, the mesh size of which is within the limits 4 to 100 mesh.

Hydrogenator 10 is equipped at 13 with a feed line and pump carrying the recycled, extracted and dried working solution for inclusion in the cycle. The hydrogenator is also equipped with means for admitting hydrogen gas. It is here shown as being admitted directly to the hydrogenator rather than being introduced into the working solution ahead of the hydrogenator. In the operation as shown, gaseous hydrogen is present in the top of the hydrogenator and in direct contact with the surface of the working solution. Hydrogenator 10 is also shown as equipped with a discharge 16 and a conduit 17 for carrying hydrogenated solution for subsequent treatment, namely, to an oxidizer (not shown), and then to an extractor (not shown).

Discharge conduit 16 is also provided with a recycling conduit 18 which is provided with a heat exchanger 19, whereby a portion of the discharge from hydrogenator 10, i.e., hydrogenated working solution, may be passed through the cooler 19 and enter the hydrogenator to mix with the fresh feed, so that now the feed to the hydrogenator comprises a portion of fresh, unhydrogenated working solution, and a portion of solution which has been hydrogenated. In this process, it is advantageous to recycle a large proportion of the effluent from the hydrogenator, as it has been found that more efficient use of the catalyst for its intended purpose is thereby obtained. The flow rate should be within the range 20 liters per square foot of catalyst cross-sectional area per minute to 200 liters per square foot per minute.

The following is a specific example illustrating the operation of the process in which the working material was a mixture of 2-ethylanthraquinone and its tetrahydro derivative.

FIGURE 2.4b: FLOWSHEET OF THE FMC PROCESS



Source: D.H. Porter, U.S. Patent 3,009,782, November 21, 1961

The working solvent consisted of approximately 60% by volume of dimethylnaphthalene and 40% by volume of trioctyl phosphate and contained in one liter, 105 grams of working material. The working material was approximately 35% 2-ethylanthraquinone and 65% of the tetrahydro derivative, after a considerable period of use.

The working solution was passed over a fixed bed of catalyst which comprised supported metallic palladium on alumina at an average particle size of 10 mesh. This catalyst had been regenerated several times to a constant activity. After 1,152 hours of use, the loss in total active quinone was found to be less than 1.0%. The cycle flow rate was 0.670 liter per minute. The overall average of recycled solution of this fluid was based on feed about 12:1, or 7.7% of the feed constituted fresh solution. By this means, the flow rate through the catalyst bed was maintained at 110 liters per minute per square foot of cross-sectional area. During the 1,152 hour operation, there was produced 370,000 grams hydrogen peroxide. The loss of usable total quinone corresponded to less than 0.001 gram per gram of hydrogen peroxide produced. These results show strikingly that overhydrogenation was maintained at a minimum, even though operating at a high hydroquinone concentration. In general, in accordance with the present operation, the feed to the hydrogenator comprises from about 1% to 50% or more fresh solution, the remainder being obtained by recycle.

Fixed Bed Hydrogenation Catalyst Consists of Noble Metal on Carrier Having Minimum Microporosity and Low Surface Area

FMC; Kreuz, D.F., and Darbee, L.R. (26): Whereas it has been generally understood until now that a fixed catalyst bed operation in the hydrogenation stage would require a larger particle size, and since the surface area is inversely proportional to the particle size, such operation would involve either a greater contact time with the catalyst or the employment of a greater weight of catalyst per unit of working material, both of which are conditions favoring unwanted hydrogenation reactions with production of degraded products. This process provides means for circumventing these difficulties.

In this process a carrier for the metallic catalyst is chosen within the range 4 mesh to 60 mesh and possessing very specific surface characteristics. Thus for fixed bed operations in the hydrogenation stage of the anthraquinone process, it is desirable that the so-called microporosity be as small as possible and generally be less than about 0.03 cc. per gram. The microporosity is defined as the volume of pores of less than 800 A. diameter. This characteristic can be measured by the method of Benesi, Bonnar and Lee, Anal. Chem., vol. 27, p. 1963 (1955) "Determination of Pore Volume of Solid Catalysts".

This requirement of a minimum of microporosity is in direct contrast with the requirement that this characteristic be present in catalyst carriers employed in fluidized operations where the catalyst is suspended in the stream of the working solution. In addition to low microporosity, the catalyst carrier should possess a relatively low surface area, in general a surface area of less than 5 square meters per gram.

As hydrogenation catalyst, one of the noble metals is employed, as for instance palladium carried upon a support possessing the characteristics mentioned. Since palladium is the best known of the noble metals of the so-called platinum and palladium group, suitable for use catalytically to aid the reaction, quinone to hydroquinone, palladium is illustrated here as the catalyst employed, similar results being obtainable for the other noble metals.

In the table below there is listed a series of catalysts, together with a notation of the surface area and the pore volume, the surface area being expressed in square meters per gram, the pore volume being expressed in cc. per gram. Each of the catalysts contained 0.5% to 1% palladium by weight and was prepared by depositing palladium chloride on carrier material which ranged in particle size from about 4 to 60 mesh, with the bulk of the carrier having a particle size of 10 to 20 mesh, and subsequent reduction of the palladium salt to the free metal.

Sample	Surface Area, per gram	Pore Volume, per gram
A. Alpha-Alumina	1 sq. meter	Less than 0.001 cc.
B. Gamma-Alumina	210 sq. meters	0.145 cc.
C. Periclase (MgO)	less than 2 sq. meters.	0.003 cc.
D. SiO_2 Al_2O_3 (85%–15%)	40 sq. meters	0.095 cc.
E. Calcium Carbonate	1 sq. meter	0.004 cc.
F. SiO_2 (low surface)	less than 2.5 sq. meters.	less than 0.001 cc.
G. Silicon Carbide	1 sq. meter	0.001 cc.
H. Magnesium Carbonate	1 sq. meter	0.002 cc.

Contrary to the indications in the prior art that the carrier composition affects catalyst activity, the example below shows that excellent hydrogenation results, and therefore production of hydrogen peroxide can be obtained, with a diversity of catalyst carrier composition. In fact, the important feature resides in providing not "an active microporous surface", but rather one that may be designated as relatively smooth.

The following is an example of the process. 3.0 liters of a palladium on gamma-alumina catalysts (B in the table above) was placed in the fixed bed hydrogenator section of a cycling system composed of the stages previously described. The working solution charged into the reactor was composed of a mixture of approximately equal amounts of 2-ethylanthraquinone and its tetrahydro derivative dissolved in a mixture of dimethylnaphthalene and trioctylphosphate. The work solution contained 0.45 mol of quinone per liter of solution.

The hydrogenation was carried out at 2 atmospheres hydrogen pressure and 45°C. to 50°C. The ratio of the total flow of work solution over the catalyst to the forward flow of work solution through the reactor could be regulated to provide any depth of hydrogenation desired. The system was operated in such a manner that the rates of reaction of quinone to hydroquinone and hydroquinone to degradation products could be determined separately. The ratio of these rates was found to be $1:186 \times 10^{-4}$. This corresponds to a loss of quinone of 9.3 mols per 1,000 mols of 100% peroxide produced, when the depth of hydrogenation is regulated to 50% of the total quinone present in solution.

Better Cementing of Noble Metal Catalyst to Carrier Is Achieved by Use of Dolomite

FMC; Darbee, L.R., Kreuz, D.F., and Jenney, T.M. (27): The catalysts which have been employed most generally comprise the so-called Raney nickel and noble metals, i.e., platinum, rhodium, and palladium, particularly the latter. In the case of Raney nickel, the hydrogenation can be directed almost entirely to the reduction of the quinone group rather than to nuclear hydrogenation of the particular anthraquinone working compound, by employing amines and other compounds to control the hydrogenating action of the Raney nickel. The particular compounds used to control the hydrogenation action of the Raney nickel are taught in U.S. Patents 2,730,533, 2,720,532, 2,730,531, and 2,756,243. However, Raney nickel catalysts are very readily poisoned by oxygen and hydrogen peroxide. Thus, the working solution must be subjected to extremely involved filtration and extraction procedures to remove traces of hydrogen peroxide or oxygen prior to being recycled to the hydrogenator. Further, nickel catalysts cannot be regenerated and accordingly must be replaced as soon as the activity falls off.

In an effort to overcome the serious disadvantages of Raney nickel, U.S. Patent 2,657,980, issued to Sprauer, teaches that palladium deposited on an activated alumina carrier gives acceptable conversion of the quinone group to the hydroquinone substituent, without being sensitive to residual hydrogen peroxide or oxygen present in the working solution. Additionally, this palladium catalyst can be readily regenerated when its activity falls off. However, this catalyst has been found to produce undesirable side products which are incapable of producing hydrogen peroxide upon cyclic reduction and oxidation. Operation in fixed beds, where the catalyst is suspended on a fixed screen or support, appears to aggravate this condition.

It was previously found that palladium supported on an alkaline earth metal carbonate makes an excellent catalyst; this reaction is one in which hydrogenation takes place quickly, smoothly, and with a high preferential reduction of the quinone group with an unexpected minimum of nuclear hydrogenation.

However, one of the difficulties which has arisen in the use of these, and certain other carriers, has been in binding the noble metal catalyst to the carrier with sufficient adhesion to prevent the physical separation of the noble metal, i.e., palladium, from the carrier. This is a most serious problem since this separation destroys the catalytic activity of the catalyst, rendering it useless in the hydrogenator. This condition is particularly aggravated by the use of catalytic carriers which have a relatively low surface area, i.e., less than 5 square meters per gram, and a relatively low microporosity, i.e., less than 0.03 cc. per gram. The microporosity may be defined as the volume of pores of less than 800 A. diameter.

Methods for overcoming this physical separation within the catalyst have been attempted but have not been proven successful, primarily because the methods employed in reducing the amount of physical separation also diminish, or even eliminate, the desirable properties of the catalyst. For example, greater tenacity between the carrier and the noble metal may be accomplished by initially etching, or otherwise producing, irregularities on the surface of the catalytic carrier prior to adding the noble metal. The result of these treatments, however, is a corresponding reduction in the high, preferential hydrogenation of the quinone group in contrast to nuclear hydrogenation. As a result, prior workers had to accept this catalyst-carrier separation as a natural incident in computing catalyst life and in determining the acceptability of a particular carrier.

It has now been determined that an excellent catalyst for the hydrogenation step of the anthraquinone process may be prepared by employing a noble metal supported on dolomite. A tenacious bond is formed between the noble metal and the inert dolomite carrier which is not subject to breakage under normal handling and use. Further, this particular catalyst has been found to have more selective hydrogenation properties than other alkaline earth metal carbonate carriers which of themselves constitute a class of highly improved catalytic carriers, possessing selective hydrogenation advantages over the prior art.

The bonding is rather unexpected because none of the other alkaline earth metal carbonates possess this high degree of adhesive tenacity which dolomite exhibits toward noble metals. While the exact reason for this unusual tenacity is not known, it is believed that it may be due to a molecular attraction between the noble metal and the surface of dolomite's unique crystal structure. That is, the dolomite crystal contains both calcium and magnesium cations in combination with the carbonate, while other readily available alkaline earth metal carbonates, in contrast, are confined to but one metal cation. However, regardless of the understanding of this effect, dolomite still stands out as the only one of this class of alkaline earth metal carbonates which have this property.

In order to produce this catalyst, dolomite, which is obtained as a naturally occurring rock, is ground to the desired fineness, as for instance about an average of 2 to 65 mesh, and preferably about 8 to 24 mesh, where the catalyst is employed in a fixed bed. When the catalyst is employed as a suspension in the flow stream, that is a so-called fluidized catalyst,

it is ground to rather extreme fineness. After this simple preparation, the dolomite is impregnated with any of the noble metals, i.e., palladium, generally by treating the material with a soluble palladium salt, and subsequently reducing the palladium salt to metallic palladium in the known and conventional manner. The finely sized catalysts so prepared may be suspended in the working solution to be hydrogenated, or in large sizes may be supported on a fixed bed. The working solution is then hydrogenated in contact with this catalyst.

Mere contact of the catalyst, working solution and hydrogen gas, at suitable temperatures and pressures, i.e., temperatures in the neighborhood of room temperature, 20° to 50°C., and preferably 20° to 45°C., are employed during the hydrogenation step. When employing palladium upon a carrier of dolomite, the hydrogenation proceeds quickly, smoothly and with a high preferential reduction of the quinone group with a minimum of nuclear hydrogenation, particularly when the hydrogenation is carried out to somewhat less than the theoretical 100% reduction. A detailed description of a conventional hydrogenation technique can be found in the Bibliography of Scientific and Industrial Research by the U.S. Dept. of Commerce, Office of Technical Science, P.B. Reports 395 and 4336.

Particular advantage of the preferred catalyst of the process, that is, metallic palladium upon dolomite as a carrier, resides in the ability of this catalyst to resist separation of the metallic palladium from the dolomite carrier and to prevent the sloughing off of the palladium metal when the catalyst is subject to normal impact during handling and use. An ancillary advantage of this catalyst resides in its control of the depth of hydrogenation of the quinone group; that is, the quinone group can be reduced substantially to the hydroquinone group with a minimum of over-hydrogenation of the quinone group, thereby minimizing any resulting loss of working material and substantially eliminating the production of undesirable and unwanted by-products possessing no efficacy as a working material since their characteristic of undergoing additional cyclic oxidation and reduction has been lost.

In the table below is indicated the change in usable mols of the working material (in this instance 2-ethylanthraquinone) per 1,000 mols of hydrogen peroxide produced, when hydrogenated to conventional depth of 50% in a solution carrying 6% 2-ethylanthraquinone and 6% 2-ethyl tetrahydroanthraquinone. The hydrogenation was performed at a temperature of 45° to 50°C. and at a hydrogen pressure in the range of 28 to 35 lbs./psi absolute. The catalyst was palladium and was placed on the specific carrier specified in the table below in amounts of from 0.2% to 0.5%, the carrier size being 8 to 20 mesh. The working mixture was a mixed solvent comprising trioctyl phosphate as the solvent for the hydroquinone form of the working material, and dimethylnaphthalene as the solvent for the quinone form of the working material. Comparative results, illustrating the favorable action of dolomite as a catalytic carrier, are shown below.

Catalyst	Carrier	Total Loss in Moles Reusable Working Material
Palladium, 0.5%	Dolomite	0.03
Palladium, 0.3%	Marble	0.65
Palladium, 0.5%	Calcium Aluminum Silicate	3.90
Palladium, 0.3%	Activated Alumina	4.95
Palladium, 0.5%	Activated Alumina	5.50

Addition of Ammonia Increases Hydrogenation Catalyst Activity Several Times

FMC; Käbisch, G., and Herzog, H. (28): After the extraction of hydrogen peroxide with water, it has been found, that when alkaline-reacting substances which are water-soluble, rather than water-insoluble, are added to the work solution, particularly ammonia, ammonium salts, or water-soluble amines, the activity of the hydrogenation catalysts is increased several times. This discovery is surprising, in that it was previously assumed that such compounds poison the catalyst. Along with the quite considerable increase in activity of the hydrogenation catalysts which is obtained with the process, there is also a better hydrogen utilization, a lesser aluminum oxide requirement, and a smaller loss in work solution by the formation of by-products. That is, all of the principal cost items of the process are reduced.

The alkaline-reacting water-soluble substance suitable is employed in the process in a concentration within the limits of 1×10^{-6} to 1×10^{-1}, and preferably 1×10^{-4} to 1×10^{-2}, mols per liter of work solution.

In determining the amount of water-soluble alkaline-reacting substances to be used in the work solution, it should also be considered that use of too much of the additive makes it possible for the hydrogen peroxide taken off in the extraction stage to become alkaline; this favors decomposition of the peroxide product. The maximal amount added should be that at which the pH value of the hydrogen peroxide remains below 8. This amount depends on various factors, e.g., the solubility of water in the work solution, and the loading of the work solution with hydrogen peroxide, and can vary within wide limits from work solution to work solution. The following example and tables show how the activity of the hydrogenation catalyst increases when the present alkaline-reacting water-soluble substance is used in the work solution.

Lyes and alkaline-reacting salts of alkali metals and alkaline earth metals can be used as water-soluble, alkaline-reacting additives, as well as alkaline-reacting oxides, ammonia, ammonium salts and water-soluble amines. Because of good solubility in the organic work solution, water-soluble amines, ammonia and ammonium salts are especially preferred, and of these, ammonia and gaseous amines are particularly suitable because of ease of operation and the possibility of expelling the additive in the oxidation zone. The following is an example of operating the process.

One hundred cubic centimeter samples of work solution were hydrogenated in a stirring apparatus in the presence of 20 mgs. of platinum black at room temperature and normal pressure. One hundred grams of 2-ethylanthraquinone were contained per liter of work solution, dissolved in a mixture of forty volume percent of 1-methylnaphthalene and 60 volume percent of octyl alcohol. Hydrogenation activity, that is hydrogen takeup in 100 cc. of work solution per minute, is a measure of hydrogenation rate. The relative moisture of the work solution remained the same in all experiments.

Additive	Concentration (mol/l.)	Hydrogenation Activity (cc./min.)
None	None	45
NH_3	3.2×10^{-5}	60
NH_3	4.4×10^{-4}	80
NH_3	4.4×10^{-3}	108
NH_3	4.3×10^{-2}	120
NH_3	8.8×10^{-2}	170

As is seen from the preceding table, hydrogenation activity increases with concentration; at a concentration of 4×10^{-4} mols per liter, it approaches twice the value of the pure work solution.

The following table shows the influence of various alkaline substances of comparable concentration on hydrogenation rate.

Additive	Concentration (mol/l.)	Hydrogenation Activity (cc./min.)
NH_3	4.4×10^{-3}	108
$(NH_4)_2CO_3$	3.3×10^{-3}	110
K_2CO_3	3.3×10^{-3}	50
NaOH	3.5×10^{-3}	50
None	None	45

The varying effectiveness of the activators is to be attributed to their varyingly good solubility in the work solution. Still higher concentrations are obtained most readily with ammonia and amines.

OXIDATION STAGE

Slurrying the Anthraquinone Working Solution Leads to Improved Yields and Obviates H_2O_2 Concentration

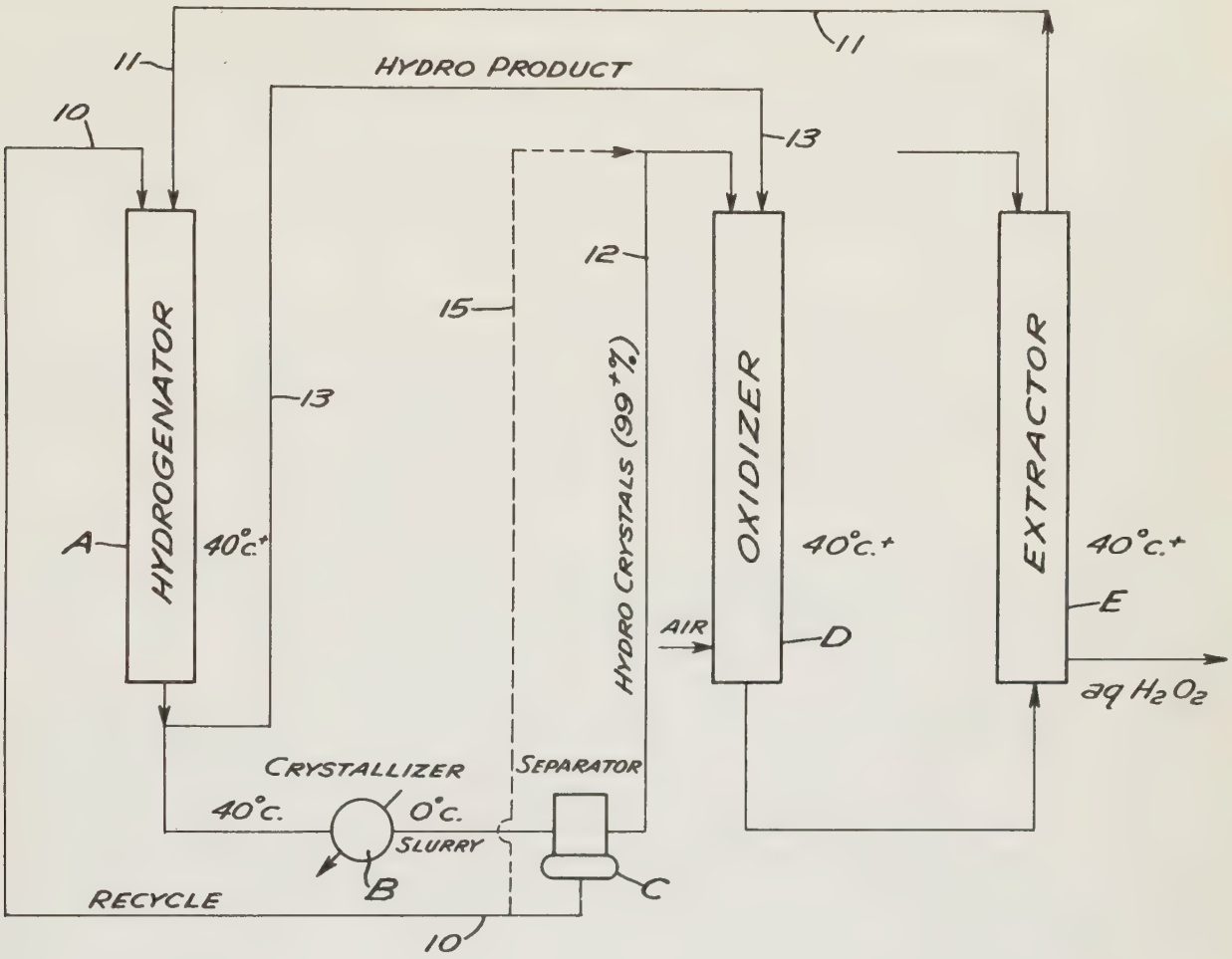
FMC; Jenney, T.M. (29): It is an object of this patent to provide greater yields of hydrogen peroxide per pass through the equipment, thereby producing an aqueous extract of hydrogen peroxide which need not be concentrated by distillation, as it is already at a recognized commercial concentration.

Figure 2.5 is a flowsheet of the process in which a hydrogenator is illustrated at A in diagrammatic form, a cooler and crystallizer at B, a crystal separator at C which may be a filter, thickener or centrifuge, an oxidizer at D and an extractor at E.

The working solvent comprises any of those solvents known to be solvents for the quinone form of the working material, such as dimethylnaphthalene, diphenyl, anisole, benzene or toluene, the preferred solvent being an alkylated naphthalene, and those solvents known to be solvents for the hydroquinone form of the working material, organic phosphate esters, organic phosphonate esters, C_7 to C_{11} aliphatic alcohols and water immiscible ketones and ethers. Generally, however, the solvent constituent for the hydroquinone form of the working material is very materially reduced and even eliminated.

The working material may be any of the alkylated anthraquinones so far employed in the anthraquinone process, such as methyl-, ethyl-, propyl-, tertiarybutyl-, or mixtures of these materials with themselves or with their tetrahydro derivatives. In general, the working solution of the process will contain from 4 to 24% of working material in the hydrogenator A. In the process, this working solution is passed to the hydrogenator and is there treated with gaseous hydrogen at conventional pressures generally employed for hydrogenation

FIGURE 2.5: PRODUCTION OF HYDROGEN PEROXIDE BY SLURRYING THE ANTHRAQUINONE WORKING SOLUTION



Source: T.M. Jenney, U.S. Patent 2,966,398, December 27, 1960

in the anthraquinone process, say one to 20 atmospheres, at a temperature of generally from about 40° to 60°C. until the solubility limit of the hydroquinone so formed is reached. Since the solubility of hydroquinone in the working solution employed in this process is somewhat lower than the solubility of hydroquinone in the conventional mixed solvents, a lower concentration of the hydroquinone form of the working material is maintained in the hydrogenator; hence the adverse effects of so-called overhydrogenation with loss of reusable working material is substantially reduced.

In the next stage, the hydrogenated working solution is withdrawn from the hydrogenator A and, in one modification of the procedure, a portion is sent to a cooler and crystallizer B where the temperature of the working solution is reduced. The reduction in temperature is sufficient to crystallize and precipitate some hydroquinone form of working material from

solution. The temperature reduction is generally from 10°C. to about 30°C. below that of the temperature in the hydrogenator. Such precipitated crystals are sent to separator C, which may be a centrifuge, to separate working solution therefrom to produce a slurry of such crystals.

In another modification, all of the effluent from hydrogenator A is sent to the crystallizer B and separator C, the crystals carrying enough entrained solvent for solution of the quinone form of the working material produced in oxidizer D. The separated mother liquor from separator C is returned to hydrogenator A through line 10 and becomes a part of the feed in the cyclic process to the hydrogenator, the remaining part of the feed coming from extractor E through line 11.

The heavy slurry of crystals of the hydroquinone form of the working material is fed to oxidizer D through line 12, where oxidation of the hydroquinone form of the working material to the quinone form occurs merely by contact with air or other convenient sources of oxygen with production of hydrogen peroxide and the quinone form of the working material, both of which end products are soluble in the working solvent. The portion of discharge from hydrogenator A, not sent to the cooler and crystallizer, is sent directly to the oxidizer D through line 13 and its amount is determined as that amount sufficient to dissolve the quinone form of the working material resulting from the oxidation of the hydroquinone form carried into the oxidizer D through lines 12 and 13. If additional solvent is required in oxidizer D, it may be obtained from the separator through line 15.

The speed of the oxidation is substantially the same as that which occurs in the homogeneous working solution heretofore treated in the oxidizer. Whereas in typical operations as performed until now, a concentration of hydrogen peroxide of approximately one gram per liter was produced, it is now possible to obtain concentrations of hydrogen peroxide as high as three grams per liter. When such a solution is treated in the extractor E, a final aqueous extract of about 50% H_2O_2 by weight results, in contrast with weight concentrations of 20% attainable previously.

In the following example, a mixed solvent of approximately 4 parts by weight of dimethylnaphthalene and 3 parts by weight of trioctylphosphate containing 12% by weight of 2-ethylanthraquinone was hydrogenated at 40°C. to the usual 50% hydrogenation depth. When two-thirds of the hydrogenated working solution was cooled and crystallized, there was sent to the oxidizer six pounds of the hydroquinone form for each 100 pounds of hydrogenated working solution and 4 pounds of hydro form from the crystallizer. There was recycled from the separator C, 176 pounds of working solvent, 12 pounds of 2-ethylanthraquinone and 8 pounds of the hydro form.

The oxidizer received 104 pounds of each 300 pounds of product from the hydrogenator, i.e., 88 pounds of solvent, 10 pounds of the hydro form of the working material and 6 pounds of unhydrogenated working material. The oxidizer discharged as product, 16 pounds of 2-ethylanthraquinone, 88 pounds of solvent, and 1.4 pounds of hydrogen peroxide, which product when extracted with 3.3 pounds of water gave 4.7 pounds of aqueous hydrogen peroxide of 30% strength. This concentration of hydrogen peroxide (1.3%) in the product sent to the extractor is in contrast with the usual 0.8% in operation where the hydro form is maintained in solution.

Carrying out the Oxidation Stage in a Slurry of Solid Anthraquinol Suspended in a Solvent with Preferential Solubility for the Anthraquinone Form

Pittsburgh Plate Glass Co.; Broun, Jr., T.T., Mares, J.R., and Raetzsch, C.W. (30): Until now, it has been proposed to dissolve a quinone, such as dimethylanthraquinone, ethylanthraquinone, tertiary butylanthraquinone, etc. or their tetrahydro derivatives, in a water immiscible solvent or mixture of solvents which is then carried through the following successive steps:

(1) Reduction of the quinone with elemental hydrogen in the presence of a suspended catalyst to produce the corresponding quinol.
(2) Separation by filtration of the suspended catalyst from the solution.
(3) Oxidation of the filtered solution with elemental oxygen (in the absence of catalyst) to evolve hydrogen peroxide and regenerate the quinone.
(4) Extraction of the hydrogen peroxide formed in step (3) with water and separation of the aqueous phase containing the hydrogen peroxide from the nonaqueous phase containing the carrier in solution which consequently repeats the cycle with step (1).

In this sequence it is important that the catalyst is carefully removed from the organic solvent after the reduction step and before oxidation, otherwise it acts to induce unwanted reactions in the oxidation step with consequent loss of yield of peroxide. Inasmuch as the catalyst is made by precipitating palladium, for example, on a granular solid such as alumina, it is necessary to remove, before using, any fines that would not be removed in the catalyst separation step (2) above and also guard against the generation of fines as by abrasion or attrition during its normal use.

Furthermore, in selecting the solvent system and in view of the filtration step, it is important that the solvent be of a character as to hold the carrier in dissolved state not only in the quinone form but also in the reduced form of the quinone. The term "quinol" is used herein to cover the reduced form of the quinone and to include both the quinhydrone in which but one >C=O group has been reduced and the hydroquinone in which both >C=O groups have been reduced. Equally important: the solubility of the aqueous peroxide, resulting from step (4), in the solvent must be low, and the solubility of the solvent in the aqueous hydrogen peroxide must be low. Otherwise, loss of production and contamination of hydrogen peroxide products will result.

A better appreciation of the problem of selecting a solvent for the quinone is illustrated in the case of a system in which dichlorobenzene is the solvent and 2-ethylanthraquinone the carrier. These data are extended to include the tetrahydroethylanthraquinone and the corresponding quinols which are usually present during normal usage. In fact, these hydrogenated quinones are useful and for most purposes satisfactory equivalents, inasmuch as they are reduced by hydrogen to form quinols and these, in turn, react with oxygen to form peroxide. The solubility of the carrier in orthodichlorobenzene, expressed as grams per liter of solution, is:

2-ethyl anthraquinone	270
2-ethyl anthraquinol	5.5
Tetra hydro-2-ethyl anthraquinone	250
Tetra hydro-2-ethyl anthraquinol	19

The marked difference in solubility of the carrier when in the quinone form from that in the quinol form has led to the use of mixed solvents, notably mixed aromatic hydrocarbons alone or in conjunction with ketones, alcohols or esters, in order to keep the quinol in solution. This in turn results in more dilute aqueous peroxide and introduces a contamination problem in step (4).

This process provides greater latitude in the selection of the nonaqueous solvent for the carrier to achieve high volume production in relation to the plant size, and makes possible the manufacture of hydrogen peroxide of any convenient concentration which may, if desired, be as high as 30 to 50% H_2O_2 by weight or higher, with lower losses of product and less contamination of aqueous peroxide by organic solvent contaminants. In the process hydrogen peroxide is prepared by reacting oxygen with a quinol in solid state. This may be done by introducing oxygen (including air) into a slurry of a solid quinol, such as solid 2-ethyl anthraquinol or like anthraquinol, suspended in an organic liquid. By virtue of this treatment, the quinol in solution is converted to the corresponding quinone and hydrogen peroxide is generated. As the dissolved quinol is converted to quinone, solid quinol dissolves, thus becoming available for reaction with further oxygen.

According to a further embodiment of the process, the quinol in solid state may be suspended in a solvent which has a substantially greater solubility for the corresponding quinone than for the quinol. In such a case, the amount of quinol suspended in the solvent is substantially above the solubility of the quinol therein, but is maintained below the concentration which corresponds in weight to the amount of the corresponding quinone in a saturated solution of the solvent. Thus, when the solid quinol is converted to the quinone, the resulting quinone dissolves substantially completely. This is especially advantageous, since the resulting solution may be extracted with water to remove hydrogen peroxide and separated from the resulting solution more readily and more completely than in the case where the solid quinone must be separated from aqueous hydrogen peroxide.

The solid quinol may be prepared in any convenient manner. For example, a solution of a quinone, such as 2-ethylanthraquinone, in an equivolume mixture of xylene and methyl cyclohexanol, may be hydrogenated to evolve the corresponding quinol and a portion of the solvent evaporated to produce a slurry containing the quinol in solid state suspended (as distinguished from dissolved). Alternatively, hydrogenation of a solution containing a high concentration of the quinone may be conducted until the amount of quinol therein appreciably exceeds the solubility of the quinol, and the quinol precipitates. Preferably, the concentration of hydroquinone in solution and the degree of hydrogenation is such that the amount of precipitated quinol is at least one half of the amount dissolved.

There are a number of solvents which are capable of dissolving substantially larger amounts of the quinone than of the corresponding quinol. For example, the solubilities of the quinol (or hydroquinone) produce by hydrogenation of a solution containing the amount of anthraquinone in grams per liter set forth in the table, dissolved in a solvent mixture of 60% by volume diisobutyl carbinol and 40% by volume alphamethylnaphthalene at 30°C., as indicated in the following table.

Starting Anthraquinone	Starting Concentration of Anthraquinone, grams per liter	Solubility in grams per liter of the Anthrahydroquinone
2-ethylanthraquinone	100	52
2-isopropyl anthraquinone	175	43
2-secondary butyl anthraquinone	175	80
2-tertiary butyl anthraquinone	175	114

Other solvents which have higher solubility for the quinone than for the quinol are: chlorobenzenes, such as o-dichlorobenzene, trichlorobenzene; chloroaliphatic hydrocarbons, such as a perchloroethylene, tetrachloroethane or ethylene dichloride; aromatic hydrocarbons, such as benzene, xylene, sec-butyl benzene, toluene, ethyl benzene, triethyl benzene or alpha methyl naphthalene, tetrahydronaphthalene and the like; ketones, such as diisobutyl ketone; ethers, such as n-hexyl ether; and esters, such as 2-ethylhexyl acetate, methylamyl acetate, methylcyclohexanol acetate or the like.

Table 2.7 shows solubilities of 2-ethylanthraquinone (EAQ) and 2-tertiary butylanthraquinone (TBAQ) in various solvents, and the solubilities of the corresponding quinol in various solvents.

TABLE 2.7: RELATIVE SOLUBILITIES OF ANTHRAQUINONES AND ANTHRAQUINOLS IN VARIOUS SOLVENTS AT 25°C.

Solvent	Anthraquinone	Solubility of the Quinone Form in grams per liter	Solubility of the Quinol Form in grams per liter
Xylene	EAQ	190	1
Do	TBAQ	364	8
Toluene	EAQ	207	1
Do	TBAQ	400	9
2-Ethylhexylacetate	EAQ	55	25
Do	TBAQ	131	100
Diisobutylketone	EAQ	51	51
Do	TBAQ	118	83
o-Dichlorobenzene	EAQ	265	6
Do	TBAQ	256	19

During the hydrogenation, a side reaction tends to occur producing the corresponding tetrahydro derivative of the quinone by nuclear hydrogenation of the anthraquinone. Nearly all solvents for these tetrahydroanthraquinones dissolve much more of the quinone form than they do of the quinol (hydroquinone or quinhydrone) form.

In the process, a solution or suspension of carrier in its vehicle or solvent is intimately mixed with hydrogen, while the solution or suspension is held in contact with a catalyst of such bulk that it can be readily separated from the resulting slurry by selective settling or filtration or by other means. Thus, the solution may be caused to impinge or react while in contact with a fixed catalyst which is held within the locus of a certain prescribed area and is restricted in its movement. Because of the restricted movement of the catalyst and

the movement of the liquid, the solid precipitated quinol is separated therefrom, being carried along with the moving solvent, and is then agitated or contacted with air or oxygen. Hydrogen peroxide thus formed is recovered as an aqueous solution by countercurrent scrubbing with water. The addition of water during the oxidation step results in the direct formation of aqueous peroxide. In either case, the aqueous and nonaqueous phases are separated, after which the regenerated quinone-solvent mixture is returned to the reduction step.

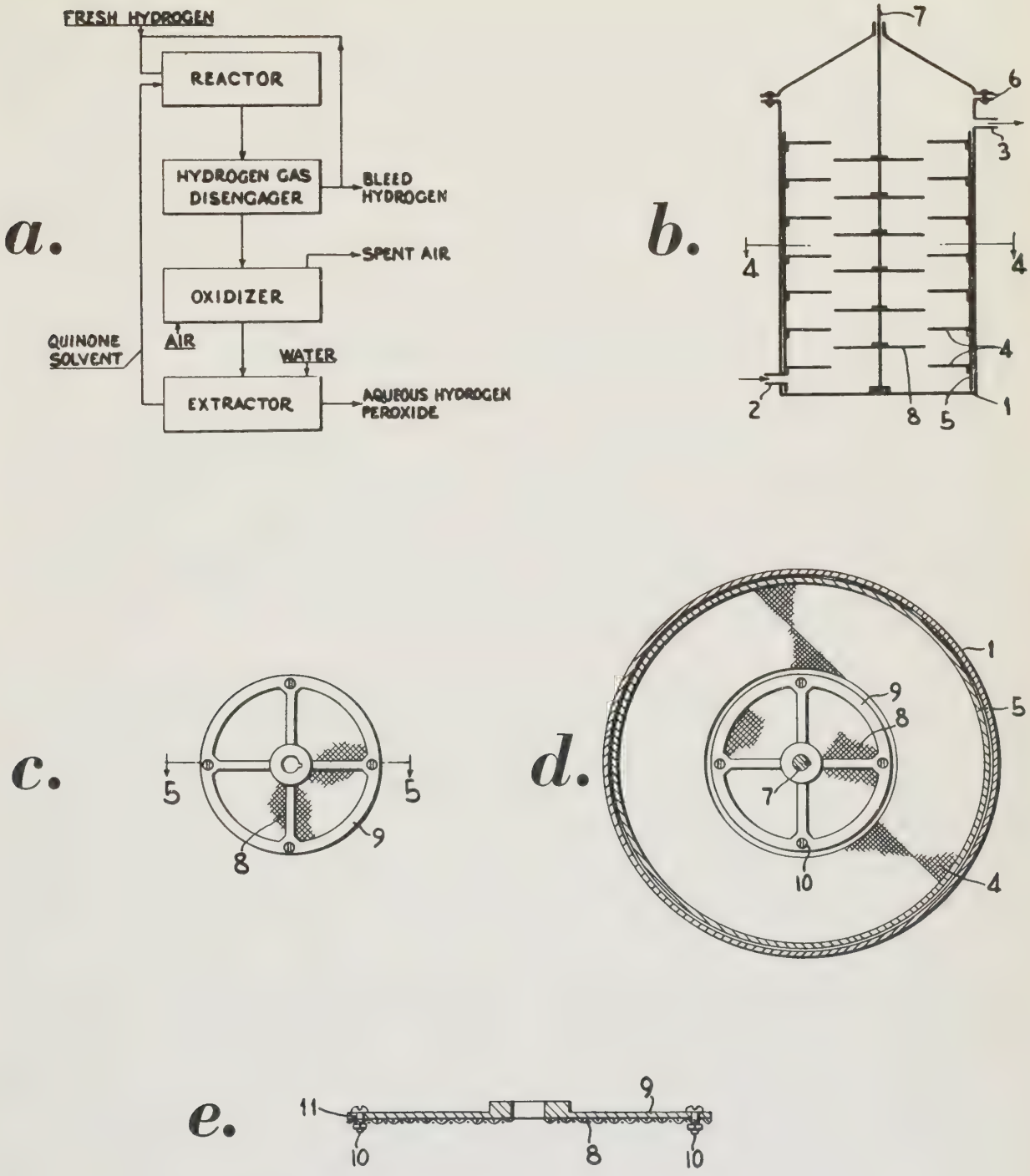
The relationship of the several steps are illustrated in Figure 2.6a, which is a general flowsheet of the Pittsburgh Plate Glass slurry process. To avoid a buildup of inert gas in the hydrogen, a bleed stream is withdrawn as indicated. According to one embodiment, the reactor may be of centrifugal pump design, built to intimately mix the gas and liquid. The impellers of the pump and the internal surface of the pump housing are plated with palladium or other catalytic reducing surface. Referring to the figure, Figure 2.6b is a vertical sectional view of a reactor for the process. Figure 2.6c is a plan view of a spider illustrated in 2.6d. Figure 2.6d is a horizontal view in section taken on line 4—4 of Figure 2.6b. Figure 2.6e is a vertical section taken on line 5—5 of Figure 2.6c.

A cylindrical vessel 1 is equipped with inlet port 2 for the liquid vehicle and the hydrogen and an exit port 3 to accommodate the reduced carrier, its vehicle, and the entrained hydrogen. A series of concentric palladium wire screen baffles 4 are secured to a liner 5 which fits inside the vessel. For ease of assembly, the head of the vessel is fabricated separately and flanged as shown at 6. A rotatable vertically mounted shaft 7 carries a series of palladium wire mesh screens 8, each secured to a spider 9 (see Figure 2.6c) which is keyed to the shaft in spaced relationship to the baffles 4 as shown. The screens are suitably secured to the spider as by means of bolts 10 which fit in holes 11 provided in the spider (Figure 2.6e). Sufficient clearance for assembly and operation is provided between the circumference of the screen 8 and the internal periphery of the screen baffle. The shaft and bearing assembly should be of such design and balance as to permit high speed rotation.

To operate the reactor, a solution containing the carrier in quinone state is introduced to partially fill the reactor, after which the agitator is started. Hydrogen is then introduced at a rate such that a mixture of hydrogen and liquid is carried out of the exit port into the disengager or entrainment separator. Subsequently, the flow of the quinone-solvent is commenced and controlled with respect to the flow of hydrogen to assure adequate residence time to reduce a substantial portion but preferably not all the quinone to quinol. When using a solvent such as orthodichlorobenzene, the reduction results in precipitation of quinol and the appearance of solids in the entrainment separator. The resulting suspension of solid quinol free of hydrogen entrainment is then subjected to oxidation by agitation with air, whereupon the solid "melts" or dissolves into solution thus indicating the conversion to quinone and hydrogen peroxide. After washing the oxidized solution with even a limited amount of water, the organic layer is freed of hydrogen peroxide and is ready to be returned to the reducer. Prior to this, it can be passed through a filter or clarifier, although under normal conditions this is not necessary.

The use of a screen or like fixed catalyst is especially advantageous when the process is conducted under the conditions described, which cause precipitation of quinol during hydrogenation. Moreover, even when operating within the solubility limits of the quinol,

FIGURE 2.6: PITTSBURGH PLATE GLASS SLURRY PROCESS FOR HYDROGEN PEROXIDE



Source: T.T. Broun, Jr., C.W. Raetzsch, J.R. Mares, U.S. Patent 2,993,760, July 25, 1961

this process avoids the difficulties of filtration, the cost of handling suspended catalyst in plant operation, and the loss of yield that results when reduction catalyst contaminates the oxidation cycle. The following is an example of operating the process.

Orthodichlorobenzene wich contains 210 grams per liter of 2-ethylanthraquinone is placed in a reactor, illustrated in Figure 2.6b, containing palladium catalyst screen, and hydrogen is bubbled into the solution while maintaining the temperature of the solution at 25°C. until about 105 grams per liter of the anthraquinone has been converted to the quinol which precipitates. The resulting slurry of precipitated quinol is introduced into a tank and air is bubbled through the slurry while maintaining the slurry at a temperature of 25° to 30°C. until the suspended solids have been dissolved. The solution is then extracted with water in the proportion of 20 volumes of solution per volume of water. The resulting solution contains about 300 grams of H_2O_2 per liter of solution.

Special Oxidation Catalysts Rapidly Oxidize Tetrahydroanthraquinone and Make Possible Utilization of the Latter as Active Constituent of the Working Material

Allied Chemical; Farrell, J.K. (31): As stated before, in the hydrogenation of the anthraquinone compound to the corresponding hydroquinone, one of the side reactions leads to the addition of hydrogen to the aromatic nucleus of the anthraquinone compound, forming the tetrahydroanthraquinone compound. In the course of repeated cyclic operations the anthraquinone compound becomes converted to the tetrahydroanthraquinone compound to an extent of sixty or more percent of the original anthraquinone compound. The formation of tetrahydroquinone has been objectionable, because it is four to six times as difficult to oxidize as the corresponding anthraquinone compound.

The effect of the presence of substantial quantities of tetrahydroquinone compound in the working solution is to seriously reduce the capacity of the plant for producing hydrogen peroxide and may mean the difference between running the operation at a loss or profit. The art recognized the problem of tetrahydroanthraquinone formation in the hydrogen peroxide process, and considerable work has been done in an attempt to minimize this inherent difficulty. One suggestion, U.S. Patent 2,673,140, was to limit the degree of hydrogenation to a level of about 60% instead of 100% by maintaining the hydrogen gas partial pressure to 0.9 atmosphere or less. Obviously, such procedure reduces the potential hydrogenation capacity.

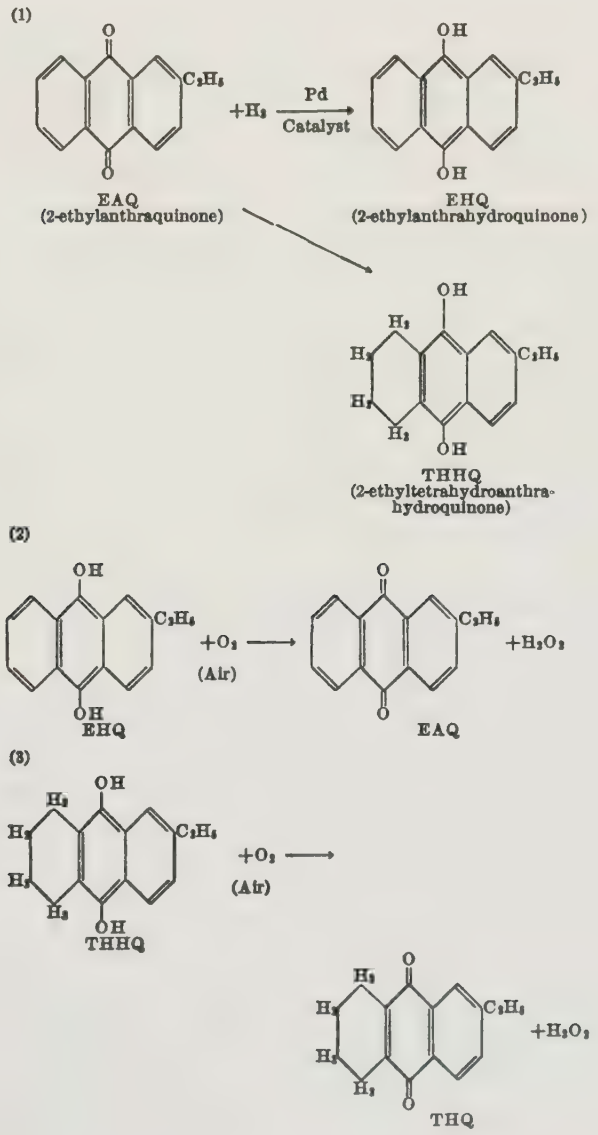
Furthermore, even at reduced hydrogenation levels tetrahydroanthraquinone continues to form at a measurable rate and accumulates in the system. Rosenmunde and co-workers found that some degree of control of catalyst activity to reduce ring hydrogenation could be obtained by the use of amines. Similar claims (U.S. Patents 2,720,531 and 2,720,532) are made for organic nitrites and nitriles. Although some reduction in the rate of tetrahydroquinone can be thus effected, the formation is not prevented and it continues to be a serious problem. In another method, as described in U.S. Patent 2,739,042, the working solution containing tetrahydroquinone was given a special separate catalytic treatment to convert it to the corresponding anthraquinone. While this method was successful in maintaining the capacity of the hydrogen peroxide process, nevertheless it entailed considerable cost for treating and converting the tetrahydroquinone.

The Anthraquinone Process

An object of this process is to provide a more efficient method of producing hydrogen peroxide via alkylated anthraquinones in which the working solution contains substantial amounts of tetrahydroquinone compound.

In the process, hydrogen peroxide is continuously produced, involving hydrogenating a working solution containing an alkylated tetrahydroanthraquinone dissolved in a water-immiscible solvent to convert the alkylated tetrahydroanthraquinone to the alkylated tetrahydroanthrahydroquinone, subjecting the hydrogenated working solution to oxidation in the presence of a small amount (preferably 0.005% to 0.02% by weight) of a water-soluble ionizable inorganic alkaline compound, with elemental oxygen in the form of pure oxygen or a gas containing elemental oxygen, to produce alkylated tetrahydroanthraquinone and hydrogen peroxide and extracting hydrogen peroxide from the oxidized solution by passing the oxidized solution in intimate contact with water.

Basic chemical reactions in the process are illustrated by the following equations:



As will be noted from Equation 1, hydrogenation of anthraquinone in the presence of a palladium catalyst produces as a primary reaction anthrahydroquinone; as a side reaction a portion of the anthraquinone is converted to the tetrahydroanthraquinone compound, as well as a very small amount of nonperoxide producing by-products of unknown composition. As a practical matter, the working solution must be recycled many times, usually five hundred or more times, thus subjecting the anthraquinone to an equivalent number of hydrogenations with consequent formation of the corresponding tetrahydroanthraquinone in each cycle; the latter accumulates in the working system, displacing the anthraquinone often to an extent of sixty or more percent.

Although the tetrahydroanthraquinone formed in a side reaction during the hydrogenation step may be used as a working compound in the hydrogen peroxide process, unfortunately the oxidation of the tetrahydroanthrahydroquinone proceeds at a rate of about one-fifth the rate at which the anthrahydroquinone oxidizes. The oxidation of anthrahydroquinone is illustrated in Equations 2 and 3 above. For example, oxidation of ethylanthrahydroquinone will occur in about three to five minutes, whereas oxidation of the corresponding ethyltetrahydroanthrahydroquinone, under the same conditions, requires twenty to twenty-five minutes. The art sought to overcome this difficulty inherent in the anthraquinone process by attempting to slow down the formation of tetrahydroanthraquinone by process control, as for example, by operating the hydrogenation step at a reduced level, i.e., hydrogenating only about 60% of the anthraquinone compound.

This process is based on a new and different approach – the utilization of the tetrahydroquinone compound as an active working constituent for production of hydrogen peroxide, without any attempt made to retard the formation of tetrahydroanthraquinone or removal of the tetrahydroanthraquinone. This is based on the discovery that the addition of relatively minute amounts of oxidation catalyst within the range of 0.002% to 0.25%, (preferably within the range of 0.005% to 0.02%, based on the weight of the working solution) to the working solution undergoing oxidation, increases the rate of oxidation of the tetrahydroanthrahydroquinone compound four to six times, e.g., it reduces the time of oxidation from about 20 to 25 minutes to about 3 to 5 minutes. Quantities of such oxidation catalyst substantially in excess of 0.25% are not effective for increasing the rate of oxidation and usually act as an accelerator to produce undesired by-products and cause decomposition of hydrogen peroxide with loss of the desired product.

The oxidation catalysts, when added to the working solution undergoing oxidation, tend to cause the formation of emulsions with the water used for extracting the hydrogen peroxide from the oxidized working solution; this is probably due to reaction with by-products to form surface active materials. The addition of an acid in an amount equal to or greater than the amount of oxidation catalyst has been found to overcome the tendency to emulsify, and the hydrogen peroxide may then be readily extracted from the oxidized working solution with water without difficulty of emulsification.

The oxidation catalysts are ionizable water-soluble compounds having an alkaline reaction. It has been found that there is a direct relation between the degree of water solubility and the catalytic effectiveness of the alkaline compound employed; the more water-soluble it is, the more effective it becomes as an oxidation catalyst. While the mechanism of the catalysis is not known, it appears that water, and/or hydrogen peroxide, is essential in

one or more steps of the oxidation using alkaline catalysts. Organic alkaline compounds are undesirable for many reasons, among which is ineffectiveness as an oxidation catalyst compared to the water-soluble ionizable inorganic alkaline compounds; they tend to contaminate the hydrogen peroxide product and complicate purification and concentration of the hydrogen peroxide product, tend to reduce the life of the palladium catalyst, and are economically disadvantageous because they are more expensive than the oxidation catalysts of this process.

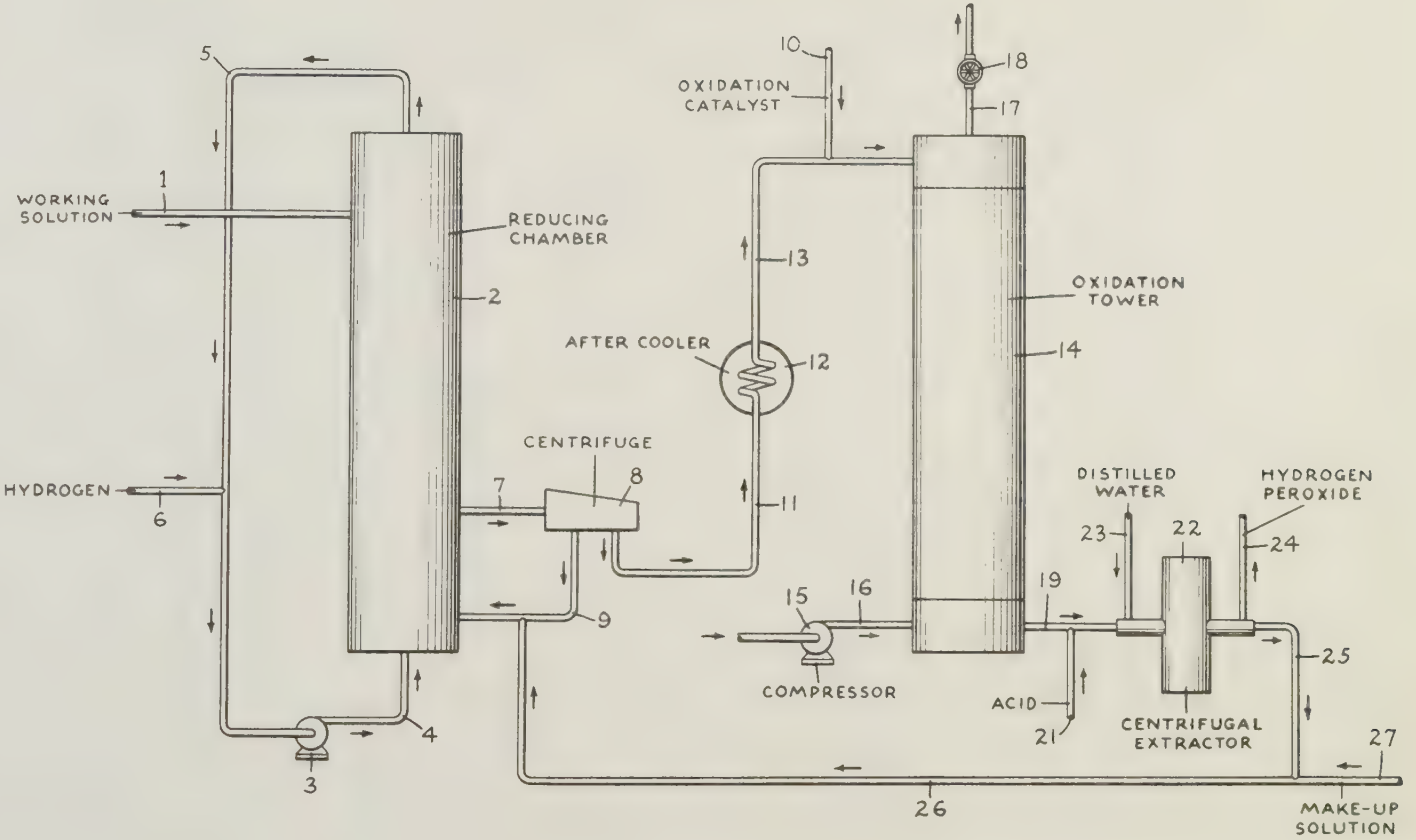
Examples of effective oxidation catalysts are ammonium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, calcium hydroxide and magnesium hydroxide. Although not preferred, barium and calcium carbonates may be employed. The preferred oxidation catalysts are the alkali metal hydroxides and ammonium hydroxide. Of these hydroxides ammonium hydroxide and sodium hydroxide appear to be best. Ammonium hydroxide is superior to sodium hydroxide, in that a smaller quantity has been found to be effective as a catalyst and additionally, ammonium hydroxide being volatile can be more readily separated from the reaction products.

Figure 2.7 diagrammatically illustrates one method of carrying out the process. A working solution is first prepared composed of a quinone compound dissolved in a solvent medium, preferably a mixed solvent with three constituents consisting of a constituent capable of dissolving the quinone such as an aromatic hydrocarbon, e.g., xylene, a constituent capable of dissolving the hydroquinone formed, such as an alcohol, e.g., octanol-2, and a synergistic solvent, e.g., a ketone such as acetophenone. The quinone compounds used as the solute are anthraquinone and derivatives of anthraquinone such as methyl-, ethyl-, propyl-, iso- and tert.- butyl-anthraquinones, the corresponding nuclear hydrogenated anthraquinones and anthrahydroquinones. The working solution is usually composed of about 10 to 25% quinone compound, 10 to 60% ketone compound, with the balance made up of the aromatic hydrocarbon and alcohol solvents.

An example of a typical initial working solution would be 15% 2-ethylanthraquinone, 20% xylene, 40% acetophenone and 25% octanol-2. During the course of operation by reduction and oxidation to produce hydrogen peroxide nuclear hydrogenation occurs as a side reaction; and after repeated cyclic operations the tetrahydroquinone formed will increase with corresponding decrease of the anthraquinone formed in the working solution, until after repeated cyclic operations sixty or more percent of the anthraquinone compound initially present in the working solution will be converted to the tetrahydroanthraquinone form. If desired, the initial working solution may contain a mixture of anthraquinone and tetrahydroquinone compounds or may contain only tetrahydroquinone compound as a quinone constituent. The working solution in the cyclic operation will, after hydrogenation, contain the quinone compound predominantly or entirely in the anthrahydroquinone form, and after the oxidation reaction the quinone compound will be predominantly or entirely in the anthraquinone form.

The working solution is introduced through line 1 in a reducing chamber 2 maintained in a temperature range of about 20 to 50°C. under substantially atmospheric pressure of about 1 to 5 psig. To the working solution is added, through line 1, hydrogenation catalyst such as palladium or platinum, preferably palladium, disposed on a solid support. The preferred catalyst consists of about 5% palladium on a charcoal or alumina carrier. The amount of catalyst required is approximately 1 to 10% by weight of the quinone present. Hydrogen

FIGURE 2.7: ALLIED CHEMICAL PROCESS FOR HYDROGEN PEROXIDE WHICH UTILIZES TETRAHYDROANTHRAQUINONE AS WORKING MATERIAL



Source: J.K. Farrell, U.S. Patent 2,995,424, August 8, 1961

is forced by pump 3 through line 4 into the bottom of reducing chamber 2 in intimate contact with a body of working solution containing suspended catalyst. Sufficient agitation to produce the necessary interfacial area for reasonable reaction rate and to maintain necessary suspension of catalyst is supplied by circulation of the hydrogen gas stream which is released from the top of chamber 2 through line 5 to the suction side of compressor 3. The hydrogen necessary to sustain the reaction is added to the circulating stream of hydrogen via line 6. The hydrogenation reaction may be carried to a high level approaching or at the level of 100%, thus enhancing the efficiency of the operation. Previously, care had to be taken to avoid exceeding a level of about 60% hydrogenation in order to minimize nuclear hydrogenation.

The hydrogenated solution containing suspended catalyst is discharged from reducer 2 through line 7 into centrifuge 8, where the catalyst is separated from the solution and returned via line 9 to reducing chamber 2. The working solution, after removal of catalyst in centrifuge 8 flows through line 11 into after-cooler 12, where some of the exothermic heat of reaction resulting from the hydrogenation is removed by indirect heat exchange with cooling water. The cooled solution is introduced through line 13 into the top of oxidation tower 14, which desirably is a vertical column filled with packing such as Berl saddles or glass beads.

A small amount, about 0.005% to 0.02%, by weight of oxidation catalyst, such as ammonium hydroxide or sodium hydroxide may be added to the working solution through line 10 or may be introduced directly into oxidation tower 14. The primary reaction in oxidation tower 14 is the oxidation of the anthrahydroquinone compounds in the working solution to the anthraquinone form, with hydrogen peroxide splitting off during the reaction. The oxidation of the anthrahydroquinone compounds may be accomplished from below room temperature to about 40°C. or more, preferably about 25° to 35°C. Oxidation may be accomplished at atmospheric pressure and preferably under superatmospheric pressure by passing an oxygen-containing gas, preferably air, by means of compressor 15 through line 16 into oxidation tower 14. The off-gases released from the top of oxidation tower 14 through line 17 and valve 18 consist principally of nitrogen and usually contain less than 1% oxygen. The oxidation catalyst effects more complete and rapid utilization of the oxygen in the air, thereby effecting a saving in the amount of oxygen-containing gas used and also producing a substantially pure nitrogen which may be used in the plant for blanketing purposes.

The products of the oxidation reaction withdrawn from the bottom of oxidation tower 14 through line 19, containing about 1.5% hydrogen peroxide, are then subjected to water extraction to separate the hydrogen peroxide from the working solution. To negate the emulsion forming tendency of the oxidation catalyst, a mineral acid such as sulfuric acid or phosphoric acid is added through line 21 to the working solution. In practice it has been found that the amount of acid required is small; usually an amount by weight equal to and up to three to four times the amount of oxidation catalyst will be adequate; that is, stated in terms of percentage, an amount of acid based on the weight of working solution of about 0.002% to about 0.5%. Reaction products from line 16 are fed to centrifugal extractor 22 into which distilled water is fed through line 23. Contact with working solution results in a water solution containing about 10 to 20% dissolved hydrogen peroxide, together with small amounts of impurities, which is withdrawn from extractor 22 through line 24 and may, if a purer and more concentrated solution is required, be subjected to further purification

and fractionation. Working solution removed from extractor 22 through line 25 is recycled to reducer 2 via line 26. Makeup solution may be added from time to time through line 27 to replace that lost from mechanical losses and chemical degradation. The following example illustrates the process.

A working solution, comprising a mixed solvent in the proportion of 34.1 parts by weight acetophenone, 27.1 parts by weight capryl alcohol, and 23.7 parts by weight xylene, and containing as a solute 15.1% by weight of a mixture of 2-ethyltetrahydroanthraquinone and 2-ethylanthraquinone of which the tetrahydroanthraquinone constituted 61% of the total ethyltetrahydroanthraquinone and ethylanthraquinone, was subjected to repeated cyclic operations, each cycle involving hydrogenation of the working solution, oxidation of the working solution, and extraction with water of the hydrogen peroxide from the oxidized working solution. The hydrogenation reaction is carried out by passing hydrogen through the working solution containing 0.5% catalyst consisting of 5% palladium deposited on carbon carrier at a temperature of 25°C., until 1,200 volumes of hydrogen per 100 volumes of working solution were absorbed.

The catalyst was then separated from the hydrogenated working solution, and the working solution subjected to oxidation at a temperature of 30°C. by passing air up through the hydrogenated working solution until 1,000 volumes of oxygen per 100 volumes of working solution were absorbed by the working solution. The oxidized working solution was then scrubbed with water to remove the hydrogen peroxide product and the working solution returned for further hydrogenation to start another cycle.

In the above operation the time required for effecting oxidation of working solution in each cycle requires 20 to 27 minutes. In a series of comparative cycle operations, 0.03 part by weight of the working solution of sodium hydroxide was added to the working solution and subjected to oxidation. The time required for effecting the oxidation, i.e., absorbing 1,000 volumes of oxygen per 100 volumes of working solution, was 4 to 5 minutes. To the oxidized working solution was added 0.05% by weight of working solution of sulfuric acid, and hydrogen peroxide was then extracted from the working solution with water without any difficulty due to emulsification.

Tetrahydroanthraquinone Is Easily Dehydrogenated by Contacting with an Unsaturated Organic Compound in the Presence of a Catalyst

Edogawa Kagaku Kogyo Kabushiki Kaisha; Hiratsuka, K., Yonemitsu, E., and Sugio, A. (32): These workers proposed, in their previous Japanese patent application Sho 35/42,347, a process for the dehydrogenation of tetrahydroanthraquinones to anthraquinones which comprises contacting tetrahydroanthraquinones with any one compound selected from alumina, magnesia, and alumina-magnesia in spinel form; or a metal which is known to foster hydrogenation in general such as palladium or nickel supported on one of the above mentioned oxides; or a mixture consisting of these substances, and a metal oxide selected from the oxides of copper, silver, lead, mercury or manganese, at a reaction temperature from 80° to 300°C. in an environment of an inert gas.

Their present process is practiced with greater ease, compared to the above process. Another process is described in U.S. Patent 2,948,739 for the dehydrogenation of an alkylated

tetrahydroanthraquinone, in which the tetrahydroanthraquinone formed in the production of hydrogen peroxide by an anthraquinone process is dissolved in acetophenone and dehydrogenated in the presence of palladium or Raney nickel supported on activated carbon at a temperature above 150°C.

According to this prior art process, the one stage conversion of an alkylated tetrahydroanthraquinone to the corresponding anthraquinones is kept at around 30%, partly because the conversion does not exceed 40% owing to the equilibrium present, and partly because the loss of the alkylated tetrahydroanthraquinone is accelerated when the conversion draws near the equilibrium; this loss may possibly reach over 30%. The solution subjected to dehydrogenation is cooled after the first stage of dehydrogenation, oxidized with oxygen and submitted to the second stage of dehydrogenation. Thus the total conversion of 70 to 80% is attained after repeating the dehydrogenation three times. With the aim of breaking the equilibrium, which exists when a hydrogenation catalyst alone is employed, to complete the reaction and obtain a quantitative yield, the inventors proposed the aforementioned process.

In their present process, they have now found that the equilibrium is broken by removing from the reaction system the hydrogen which in turn has been removed from the tetrahydroanthraquinone. This is accomplished by introducing substances which easily react with hydrogen, such as olefins, into the reaction system, whereby the hydrogen emanating from the tetrahydroanthraquinone hydrogenates the olefins.

The process is practiced in the following way. A substance selected from alumina, magnesia, alumina-magnesia in spinel form, active carbon, or a carbonate of a metal selected from Group I or II of the Periodic Table, or a mixture of the above mentioned substances, and a metal which is known to foster hydrogenation in general such as palladium, platinum or nickel, are added to a solution comprising a tetrahydroanthraquinone. The solution is then contacted with an organic compound having at least one unsaturated bond, at a temperature exceeding 80°C., to lead the dehydrogenation to completion with a quantitative yield. In the case where an unsaturated compound is not introduced into the system and the reaction is carried out in an environment of an inert gas such as nitrogen, the conversion of the tetrahydroanthraquinone reaches only 55% and the total anthraquinone recovery is reduced to 70%.

This process is characteristic in that the reaction is completed by a simple one stage operation with a quantitative yield. Another characteristic of the process is that the working solution, employed in the production of hydrogen peroxide by the anthraquinone process, which consists of a solution comprising an anthraquinone dissolved in solvents such as hydrocarbons, aliphatic alcohols, phosphoric acid esters or acetophenone, may be submitted to the dehydrogenation process without any pretreatment. By contrast, in the processes described in U.S. Patent 2,739,042 and 2,948,739, a tetrahydroanthraquinone is extracted from the working solution prior to the dehydrogenation. The extracted tetrahydroanthraquinone can successfully be dehydrogenated by the present method.

In this process, the dehydrogenation of a tetrahydroanthraquinone is accomplished with a conversion of 100% and a quantitative total anthraquinone recovery is obtained whether a tetrahydroanthraquinone alone or a mixture of a tetrahydroanthraquinone and an

anthraquinone is submitted to the dehydrogenation, and further irrespective of the concentration of the tetrahydroanthraquinone or of the kind of the substituent alkyl radicals on the tetrahydroanthraquinone. The solvents which are applicable to the process include aliphatic or aromatic hydrocarbons, alcohols, ketones, esters and any other solvents, which are stable to usual hydrogenation catalysts.

Concerning the reaction temperature, the dehydrogenation proceeds with a fair velocity at a temperature around 100°C., in general with a sufficient velocity at the boiling point of the solvent employed. The dehydrogenation is completed in 2 hours at a temperature between 150°C. and 160°C., while the boiling points of the solvents generally employed in the anthraquinone process fall within the range of 150° to 200°C. The dehydrogenation velocity about doubles by 10°C. elevation of the reaction temperature. Though the reaction temperature is limited by the thermal stability of tetrahydroanthraquinones, the reaction may be carried out even at a temperature as high as 300°C.

As dehydrogenation catalyst, alumina, magnesia, alumina-magnesia in spinel form, active carbon, and a carbonate of a metal selected from Group I and II of the Periodic Table may be used. They are effective in the order of magnesia>spinel>alumina>active C>carbonate. As hydrogenation catalyst, a material conventionally used for this purpose, such as palladium, platinum or nickel, is applicable. Palladium is most conveniently employed, as in general this material is employed as the hydrogenation catalyst of an anthraquinone to the corresponding hydroanthraquinone in the anthraquinone process. The amount of palladium sufficient for the process is about 1% based on the weight of the carrier. The metals employed as hydrogenation catalyst can be used either in the form of a mixture with alumina, magnesia, alumina-magnesia in spinel form, active charcoal, or a carbonate of a metal selected from Group I or II of the Periodic Table, or in the form supported on one of the above mentioned substances.

The organic compounds with at least one unsaturated bond, which are applicable to the dehydrogenation process, include acetylene, ethylene, propylene, and cyclic olefins, of which ethylene and propylene are most conveniently applied as they are commercially obtainable at moderate prices. The following example illustrates the process. Here the terms are employed in the following meanings.

$$\text{Conversion} = \frac{\text{THAQ present before dehydrogenation (by mol.)} - \text{THAQ present after dehydrogenation (by mol.)}}{\text{THAQ present before dehydrogenation (by mol.)}} \times 100$$

$$\text{Conversion to anthraquinone} = \frac{\text{AQ converted from THAQ (in mol.)}}{\text{THAQ present before dehydrogenation (by mol.)}} \times 100$$

$$\text{Total anthraquinone recovery} = \frac{\text{AQ+THAQ present after dehydrogenation (by mol.)}}{\text{AQ+THAQ present before dehydrogenation (by mol.)}} \times 100$$

REMARKS.—THAQ: Tetrahydroanthraquinone; AQ: Anthraquinone.

In a flask accommodating a thermometer, a stirrer, a reflux condenser and a gas inlet, were placed 100 parts by volume of the solution which comprises 0.0665 mol./l. tetrahydrobutylanthraquinone and 0.607 mol./l. butylanthraquinone dissolved in a mixture of trimethylbenzene and diisobutylcarbinol in the ratio of 50:50 by volume. To the solution were added 10 parts by weight of Pd—$MgAl_2O_4$ (Pd 2%) as catalyst, and the solution was heated at 164° to 168°C. for 3 hours, leading a stream of ethylene gas into it under the normal pressure at a flow rate of 750 parts by volume per hour. The total volume of ethylene gas thus passed amounted to seven times as much as the quantity theoretically required. 99% conversion to the corresponding anthraquinone was attained with 100% total anthraquinone recovery.

Carrying Out the Oxidation Step in the Absence of Alkaline Catalysts, in Acid Reaction Medium, Gives Improved Yield and Minimizes Impurities

Kali-Chemie AG; Kunowski, H., and Fix, G. (33): In order to increase the rate of oxidation in the oxidation process it has been suggested to carry out the oxidation in the presence of an alkaline oxidation catalyst and to use preferably alkali metal hydroxides and ammonium hydroxide. These catalysts are used in small amounts, e.g., 0.005% to 0.02% based on the weight of the working solution. They increase the rate of oxidation, but it has been found that their presence tends to cause or increase the formation of emulsions when extracting the H_2O_2 with water from the working solution and to render separation of the working solution from the aqueous extract difficult. In order to eliminate this harmful influence of the aforementioned alkaline oxidation catalysts, it has been suggested to add to the working solution containing the alkaline catalyst, after the oxidation, a small amount of an acid, usually an amount by weight equal to and up to 3 to 4 times the amount of oxidation catalyst, prior to the extraction of H_2O_2 with water.

Contrary to the above described prior art process, it has now been found that valuable advantages can be attained by avoiding the addition of alkaline catalyst to the oxidation solution and carrying out the oxidation in an acid reaction medium in the following manner. After the hydrogenation step, acid is added to the working solution in an amount that the pH-value of the resulting aqueous hydrogen peroxide extract is below 6, preferably in the range between 2 and 4. The oxidation is then carried out in the presence of the added acid. After oxidation the working solution is extracted with demineralized water, whereby H_2O_2, the acid and metallic compounds, if present, are extracted by the water, with sharp separation of the organic solution phase and the water phase, i.e., without emulsion formation. It has been found that this procedure has the following advantages:

(a) The yield of H_2O_2 is increased.
(b) No emulsion-formation occurs.
(c) The working solution contains no metallic compounds.
(d) Losses and impurities in the working solution and the amount of impurities in the H_2O_2 extract are at a minimum.

In order to obtain an optimum effect, the solubility of the acid used should be as low as possible in the organic working solution, and as high as possible in the water used for the extraction of the H_2O_2. For the purpose of this process, any acid can be used which is practically insoluble in the organic reaction solution and completely soluble in water. Suitable acids are, for example, phosphoric acid, HNO_3, H_2SO_4, HCl, and other acids

which meet these requirements. In general the use of phosphoric acid will be preferred, because the stabilization of the H_2O_2 prior to its further processing – e.g., by distillation for obtaining a more concentrated commercial product – is effected by phosphoric acid.

The amount of acid which is to be added to the working solution depends on the volume proportion of the working solution to the water used for extraction. If one volume of working solution is extracted with one volume of water, 0.033 ml. of 0.1% phosphoric acid per 1 liter working solution is required to obtain a pH-value of 6 in the aqueous H_2O_2 extract. If it is desired that the pH-value of the aqueous H_2O_2 extract is 2 and if the proportion of working solution to water is 1:1, 330 ml. of a 0.1% phosphoric acid must be added to the working solution. When another acid is used, the corresponding chemical equivalent amount is to be used. In any case the amount of the acid should be calculated in such a manner that the pH-value of the resulting H_2O_2 solution lies under 6 and preferably between 2 and 4. The concentration of the acid used is not important. It has been found practicable, however, to use concentrations between 0.1 to 10% and not higher for ease of dosage.

The following example shows the results obtained without the addition of acid to the working solution prior to the oxidation phase. In a conventional recycling apparatus, 10 liters of a solution of 120 g. of 2-ethylanthraquinone in 380 g. of octyl alcohol and 500 g. of benzol were hydrogenated per hour, oxidized, extracted with water and subsequently subjected again to hydrogenation. Hydrogenation was carried out with Raney nickel catalyst, using 1 to 2% by weight based on the weight of the recycling solution.

Hydrogenation was continued at a temperature of 25°C. until 4 volumes of hydrogen were absorbed per volume of the recycling solution. Thereby 37.4 g./kg. ethylanthraquinone were converted into the hydroquinone form. Subsequently the catalyst was quantitatively removed, before the recycle solution which now contains 2-ethylanthraquinone partly in hydroquinone form is oxidized again by passing air through it at a temperature of 30°C. The air was conducted in excess through the solution until about 4 volumes oxygen were absorbed per volume of the recycle solution. The residence time of the recycle solution in the oxidation phase amounted to 30 minutes.

After the oxidation, H_2O_2-content of the recycle solution amounted to 4.83 g./kg. and this corresponds to a yield of 90.4% of theoretical calculated on the 2-ethylanthrahydroquinone content present after hydrogenation. Subsequently the H_2O_2-containing working solution was extracted with demineralized water. Depending on the proportion between the organic phase and the extraction water, the H_2O_2 solutions obtained are more or less concentrated. The yield in the extraction step is influenced by the known factors, such as the distribution equilibrium of the H_2O_2 between the two phases, the temperature, the number of steps of the extraction plant, etc.

In the present case, the proportion of the organic to the aqueous phase was 2:1 parts by weight. At a pH value of the aqueous H_2O_2 of 6.6, this layer had a milky turbid appearance. The aqueous solution still contained about 100 mg. organic solution/kg. The concentration of H_2O_2 amounted to 8.94 g./kg. This corresponds to a yield in the extraction of 92.5%.

In another test, in the same solvent mixture 120 g. 2-tert.-butylanthraquinone was dissolved. The process was carried out in the same manner, but the hydrogenation was carried out at about 40°C., and only 3.5 volumes of H_2 were required for one volume of working solution and accordingly one volume working solution required for oxidation only about 3.5 volumes of O_2. The difference between the hydroquinone content prior to and after the oxidation amounted to 41.5 g./kg. of working solution. After oxidation, the H_2O_2-content of the solution amounted to 4.56 g./kg. working solution. This corresponds to a yield of 86% of theoretical during oxidation. In this test, too, the proportion by weight of organic to aqueous phase is 2:1. At a pH value of the aqueous phase of 6.7, this phase was weakly milky-yellow. The aqueous solution still contained 120 mg/kg. recycle solution. The concentration of H_2O_2 amounted to 8.4 g./kg. This corresponds to a yield of 92% in the extraction.

Oxidation of Working Solution Is Carried Out as a Staged Gas-Liquid Reaction at Low Gas Compression Costs

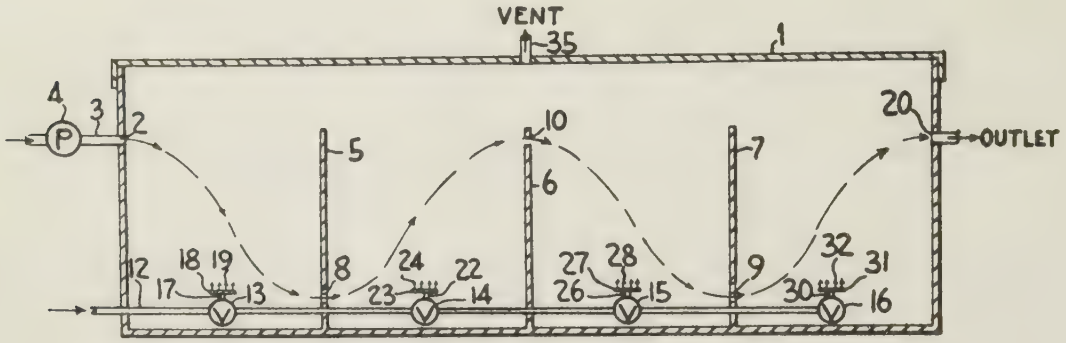
Laporte Chemicals Ltd.; Ogilvie, A., and Laurence, B. (34): This process constitutes an improvement in the oxidation step which involves feeding the solution from the hydrogenator stagewise through a series of two or more reaction compartments or vessels and feeding into the solution in each of these compartments, the gaseous oxidizing agent or reactant in a quantity which is preferably at least that theoretically required for the oxidation in that compartment of the anthraquinone fed into it.

The oxidizing gas can be one or more of air, oxygen or oxygen-enriched air. Preferably, the compartments or vessels are aligned substantially horizontally. If desired, when separate oxidation vessels are employed, the oxidized solution issuing from each vessel is passed through a corresponding degassing zone before being passed to the next oxidation vessel. It is preferred always to pass the oxidized solution from the last vessel through a degassing stage. The degassing stage can be conducted either in a separate vessel or in a suitable region of the oxidation vessel itself.

It is also advantageous to feed the oxidant gas to the solution by bubbling it into the solution at each stage through a suitably apertured ring, for example, a sparge ring. Advantageously too, the feed of the oxidant gas to each stage is individually metered, and the gas is employed in at least 100% quantities of that theoretically required for the oxidation of the solution contained in each stage, thereby providing in each stage sufficient oxidizing gas to oxidize the solution completely at each stage. For a better understanding of the process, reference is made to Figure 2.8, in which is shown a suitable oxidation vessel 1.

This oxidation vessel 1 is provided with an inlet 2 for the introduction of the anthrahydroquinone liquid, which is pumped through the line 3 by means of pump 4. The oxidation vessel 1 is provided with several partitions or baffles 5, 6 and 7. Baffles 5 and 7 are provided with a plurality of openings 8 and 9 respectively, located in the bottom of each of the partitions. A number of openings 10 are provided in the upper portion of the partition 6. Located in each compartment formed by these partitions or baffles is a common manifold or gas duct 12 for the introduction of an oxidizing gas. The manifold 12 traverses each compartment and in each compartment is located an individually controlled gas valve. These valves are designated 13, 14, 15 and 16.

FIGURE 2.8: APPARATUS FOR CARRYING OUT THE STAGEWISE OXIDATION OF ANTHRAQUINONE WORKING SOLUTION IN A NUMBER OF HORIZONTALLY ALIGNED REACTION COMPARTMENTS



Source: A. Ogilvie, B. Laurence, U.S. Patent 3,323,868, June 6, 1967

Each valve has associated with it a small tube, such as tube 17, associated with valve 13 for the transfer of gas from the manifold 12 to the associated sparge ringe 18. The sparge ring is composed of a ring of metal having a number of openings depicted by the arrows 19. At the end of the oxidation vessel opposite the inlet opening is an outlet opening 20 for the discharge of liquid introduced into the vessel.

In the use of the above equipment, the solution of hydrogenated compound from a hydrogenator is pumped into the inlet 2 utilizing pump 4 and conduit 3. The material entering the first reaction vessel or zone is oxidized by air being bubbled through the manifold 12 and by manipulation of valve 13 through conduit 17, sparge ring 18 and the openings 19. The air introduced through the openings 19 is bubbled up through the solution as it travels through the initial compartment. The solution in the first compartment is transported into the second compartment through openings 8 located in the bottom of baffle plate 5. The solution as it enters the second compartment is oxidized by the introduction of oxygen through manifold 12, valve 14, conduit 22, sparge ring 23 and openings 24. After oxidation in the second compartment, the liquid passes upwardly and through openings 10 in the baffle plate 6 located between the second compartment and the third compartment. The liquid is then introduced through this opening 10 into the third compartment, where it is oxidized further by passage of the oxygen-containing gas from the manifold 12 by manipulation of valve 15 through conduit 26, sparge ring 27 and openings 28.

After having been suitably oxidized in this compartment of the oxidation vessel, the solution passes through openings 9 located in the bottom portion of the baffle plate 7. The solution then enters the last compartment of the oxidizing vessel where it is oxidized with an oxygen-containing gas by manipulation of valve 16 at the end of the manifold 12. The oxygen-containing gas passes through conduit 32, the sparge ring 31 and the openings 32. The completely oxidized solution is then passed upwardly through outlet 20 and, after discharge,

is suitably degassed. Care must be taken in passage of the liquid through the oxidizing vessel to insure that the rates of feed and the rates of withdrawal of solution are such that the height of the solution in each compartment is less than the height of the baffle plates, so that uncontrolled overspilling from one compartment to the other is avoided. Operating in this manner, and by analyzing the solution from time to time, as it passes through each compartment, a rapid accurate control of the extent of oxidation in each compartment can be maintained.

The resulting hydrogen peroxide remains dissolved in the solution passing from the outlet 20 of the oxidizing vessel. This solution is then fed through a degasser which may either be separate from or can be if desired, incorporated into the oxidizer itself. The separation of the hydrogen peroxide from the hydrogen peroxide containing solution is accomplished in a conventional manner.

Located in the upper portion of the oxidizing vessel is a vent 35 for the discharge of excess oxygen. While not shown in Figure 2.8, if desired, gas escaping from the oxidation compartments of the oxidation vessel may be demisted by providing a blanket of suitably gas-porous material over the individual compartments formed by the baffles whereby the gas is freed from any entrained liquid, prior to its passage through vent 35. In this manner, any liquid entrained with the gas drops back into the compartment from which it escapes. Alternatively demisting can be conducted in an apparatus separate from the oxidizer. In this case, gas escaping from the oxidizing chamber through the vent 35 may be demisted in a vessel separate from the oxidizer and this solution returned to the oxidizer through inlet 2.

For a given rate of flow of a given feed solution at a definite temperature, it is possible to calculate theoretically the amount of oxidation which will be accomplished in each compartment of the oxidizer for a given oxygen partial pressure. In practice at each stage, there is normally employed an excess of air over that theoretically required for the oxidation in that stage. The excess will normally be in the order of 100% or more, but may be several times that figure if desired. It may be desirable on occasion to use less than the theoretical figure; if so, quantities usually on the order of 0.7% of theoretical are utilized. Factors which increase efficiency of oxidation are agitation of the solution in the compartments, decrease in the escape aperture size of the oxygen gas pipe, and increases in temperature. Because of the latter, the oxidizers may be advantageously provided with a steam or hot water jacket or some other suitable heating means to provide sufficient heat to increase the rate of oxidation occurring in the various compartments of the oxidizer itself.

Although the oxidizer described is in effect a single unit, divided into a multiplicity of compartments, it will be appreciated that several such compartmented units may be used. Each unit in such a case would have a feed inlet and feed outlet, and means for permitting a metered supply of oxygen gas to be released within each compartment. Conveniently the oxidizing gas can be dispersed by means of a sparge ring or other similar dispersion apparatus.

Similarly if desired, the oxidizing feeds to the various chambers or vessels used in the oxidizer may be fed from individual gas units rather than being fed from a common duct or manifold as shown in the drawing. So long as individual contact of the gas feed to each chamber or vessel is provided for, the advantages of the novel oxidizing method will be realized.

One important advantage accruing from the process such as described, is that a staged gas-liquid reaction can be conducted at low gas compression costs. This advantage is especially marked in those cases where the reaction is a slow one and several or many stages are required to achieve an acceptable degree of reaction.

EXTRACTION STAGE

Extraction of H_2O_2 from Working Solution Is Greatly Improved by Using Acidified Water

Kali-Chemie AG; Kunowski, H., and Fix, G. (35): However elegant the anthraquinone process may be considered to be, in its execution various difficulties are encountered which considerably affect the economy and use of the process. Thus, the contamination of the organic solution by small amounts of metal compounds originating from the apparatus used cannot be always safely avoided, and these compounds can attain a concentration, at which they cause catalytic decomposition of the H_2O_2 present in the organic solution. If these metal compounds, and even their traces, are not continuously removed from the organic reaction solution, the catalytic decomposition caused by them can result in a considerable reduction of the yield, and even the course of the reaction can be disturbed.

A further difficulty is encountered in the continuous extraction of the H_2O_2 with water from the organic solution. It is thereby necessary to attain practically complete extraction of H_2O_2 by the water, without the occurrence of losses of the recycled organic solution, due to emulsification in the aqueous phase. Such emulsification can be substantially avoided at the beginning of the operation by suitable selection of the organic solvents. However, after a certain period of operation, the recycled organic solution shows the tendency to form emulsions with the water used for extraction, to an increasing extent. While fresh organic solutions show practically complete separation from the aqueous phase after extraction by the latter, after increased periods of operation the separation of the organic solution from the aqueous phase becomes increasingly slower. The separating layer shows lack of sharpness and becomes indefinite and the originally clear aqueous layer becomes turbid and milky.

The formation of emulsions can be considerably reduced by increasing the extraction temperature. However, the use of increased extraction temperatures results in losses of H_2O_2, because at higher temperatures increased amounts of H_2O_2 remain dissolved in, and thus retained by, the organic reaction solution. It is possible to purify the aforementioned turbid aqueous extraction solution, e.g., by extraction with an organic solvent or by the action of a solid adsorptive agent, whereby dissolved or emulsified particles of the organic solution can be removed. However, such purification requires additional operating steps and equipment and increases the expenses of the process.

Finally, it is in many cases necessary to subject the recycled organic reaction solution prior to returning it to the hydrogenation step, to purification in order to remove from it traces of metals and other impurities entering it during its circulation. Such purification is usually carried out by washing the organic solution with water, which – after its use for purification – contains only very small amounts of H_2O_2, but may contain essential amounts of the organic solution, which are lost unless the water is further subjected to a relatively

troublesome and expensive purification. It has now been found that the above described difficulties can be avoided by using for the extraction of H_2O_2 from the organic reaction solution, demineralized water which has been adjusted to an acid pH value by the addition of an acid. It has been found that by using for extraction of the H_2O_2 water which has a pH value of less than 6, the traces of metals present in the organic reaction solution are continuously removed and simultaneously the formation of emulsions is prevented. Upon adjusting the pH of the water to a value below 6, preferably 2 to 4, and using this water for extraction of the H_2O_2, an immediate, clear separation of the organic solution from the aqueous phase takes place. Moreover, by proceeding in this manner, the removal of metals from the organic reaction solution by a separate step becomes unnecessary.

A further advantage of the process consists in that the extraction of H_2O_2 can be carried out by relatively low temperatures so that losses of H_2O_2 can be further reduced. Although the effect of temperature on the distribution coefficient of H_2O_2 between the organic and aqueous phase is influenced by the chemical nature of the organic phase, it is a generally valid rule that the yield of extraction decreases upon increase of the temperature, under otherwise equal conditions. It should be also taken into consideration that the liability to decomposition of H_2O_2 increases with increasing temperature, and temperatures above 50°C. can cause noticeable decomposition of H_2O_2. It is, therefore, desirable to carry out extraction of H_2O_2 at a temperature which is as low as possible. As the practically lowest limit of extraction temperature is determined by the temperature of cooling water — which is in general not lower than 15°C. — it is preferred to carry out the extraction of H_2O_2 in the range of 15° to 50°C.

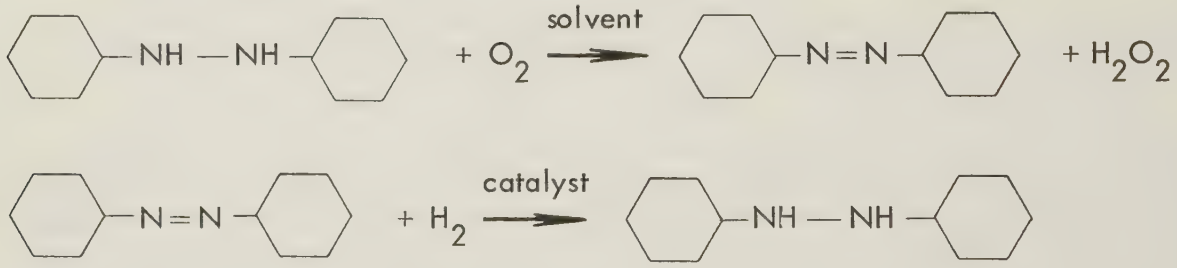
The adjustment of the pH of the water used for extraction can be carried out by the addition of an acid. In selecting the acid used for this adjustment, it should be taken into consideration that the acid should be practically insoluble in the organic reaction solution and completely soluble in water. The use of phosphoric acid for adjustment is preferred if stabilization of the H_2O_2 prior to its further processing — e.g., by distillation for obtaining a more concentrated commercial product — is effected by phosphoric acid. However, other acids, such as, e.g., HNO_3, HCl, H_2SO_4 or others can likewise be used. If — for special reasons — a separate purification with water of the recycled organic solution is carried out, the water used for such purification must be likewise acidified in the manner described above in order to remove traces of metals. The following example may clarify the process.

The working solution used is composed of 120 parts by wt. ethylanthraquinone, 380 parts by wt. octanol and 500 parts by wt. benzene. In a recycling apparatus 10 l./hr. of this solution are hydrogenated and subsequently oxidized in conventional manner. The H_2O_2 present in the solution after oxidation is extracted by 500 $cm.^3$ of water, which was freed from mineral ingredients and has a pH=7.0. After operating for 4 weeks, the Ni-content of the recycled solution increased to more than 4 ppm, while the aqueous phase contained less than 0.01 ppm of Ni. In order to free the recycled solution of Ni, which has a catalytic decomposition effect on H_2O_2, the pH of the water (which was freed from mineral ingredients) used for extraction of H_2O_2 was adjusted to 3.0 by the addition of phosphoric acid. After further operating for 8 days, the Ni-content in the organic solution decreased to less than 0.2 ppm, while it simultaneously increased in the aqueous phase to 0.5 to 1 ppm. These values did not change during further operation for more than 3 months, in which the pH of the water was kept at 2 to 4.

OTHER PROCESSES

CYCLIC OXIDATION AND REDUCTION OF HYDRAZOBENZENE

Osakeyhtio-Kymmene Aktiebolag; Ornhjelm, R.M.R. (36): It is known that alkaline peroxides can be made by oxidation of certain organic compounds such as hydrazobenzene, dissolved in aqueous alkali bearing alcoholic solutions, the molecules of these compounds having two relatively easily removable hydrogen atoms which react to form the peroxide. The latter is recovered from azobenzene which is reduced for reuse in the oxidation phase:



It will be seen that, chemically, the hydrazobenzene process is very similar to the anthraquinone process.

Proposals have been made that azobenzene be hydrogenated by means of hydrogen in the presence of a catalyst, but also in this case hydrogenation is carried out substantially with the aid of alkali amalgam, commonly sodium amalgam, which at the same time serves to provide the alkali amount requisite for the oxidation process and which is reused after electrolytical makeup of the consumed alkali metal. Peroxides may be produced continuously if the hydrogenation phase and the oxidation are carried out in one and the same cycle and the electrolytical enrichment of the amalgam with an alkali metal and reduction are carried out in a second cycle. In addition to this, the amount of active oxygen contained in the obtained peroxides may be adjusted by adding water to the oxidizing solution in amounts ranging from negligible to 8 mols per oxygen mol consumed.

Although the method as just stated has theoretically been fully explained, commercial application has not met with success due to an inability to obtain the required capacity. In all prior methods, the amalgam for the reduction phase is withdrawn from an electrolytic cell operating under conventional operating conditions and is passed through the reduction phase of the process at a rate equal to the normal rate of flow, or production of the amalgam

by the cell. Accordingly, in these methods the amount of amalgam flowing in a unit of time through the reduction phase will, at its height, equal the amount of amalgam normally formed in the cell within the same unit of time. Agitators and circulation pumps and the like, proposed for maintaining amalgam circulation, have neither been successful nor brought about any change in this respect.

It has now been found that the reduction of an azobenzene solution under the above stated conditions does not proceed sufficiently rapidly to be of importance for production purposes. The presence of considerable amounts of alkali metal in the amalgam stream cycled for make-up purposes from the reduction phase to the cell serves to prove this fact, and this could well mean that prolongation of reaction time would be desirable. Trying to effect such prolongation, however, meets with difficulties of technical nature.

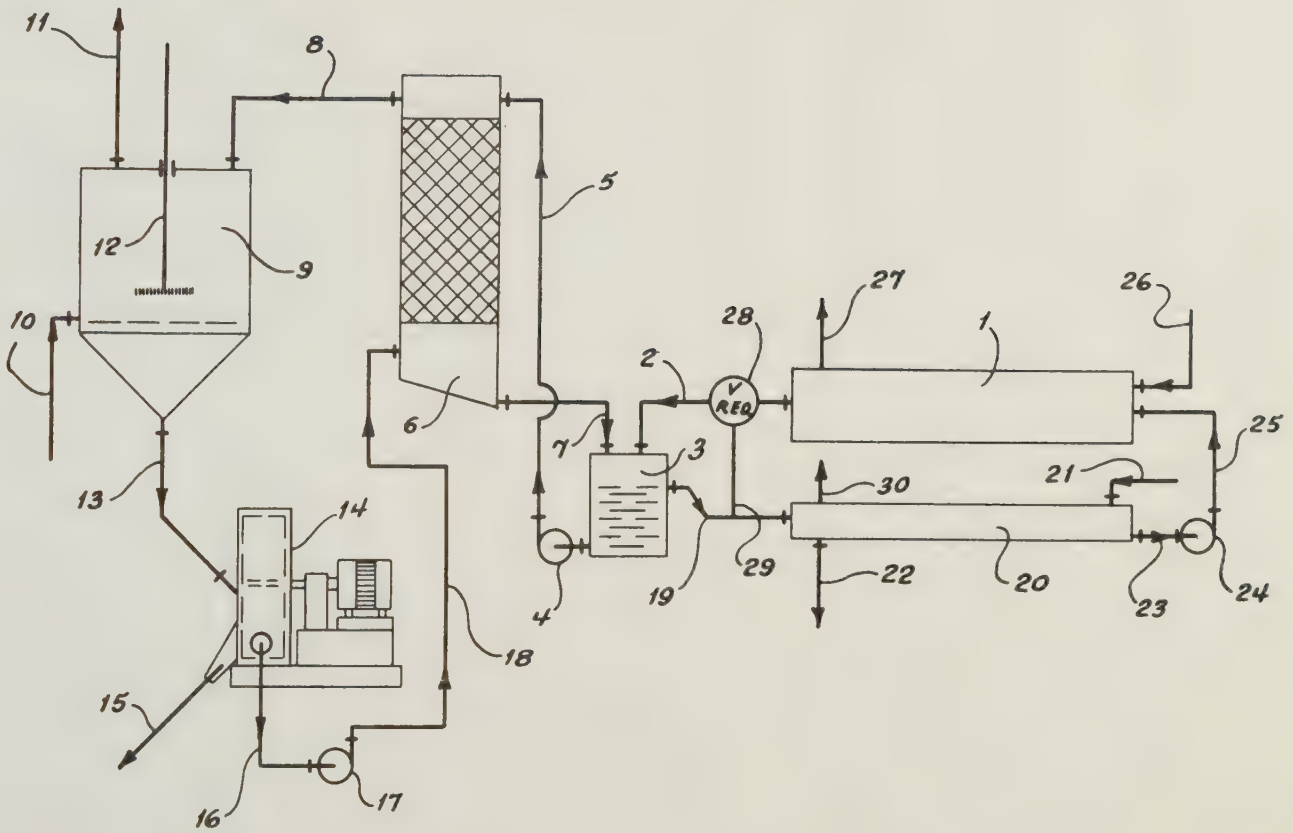
The stated shortcoming of known methods can be easily and effectively obviated by causing the amalgam issuing from an electrolytic cell to circulate with such speed that the total alkali metal contained in the amalgam passed per unit of time through the hydrazobenzene solution is equivalent to at least 1.5 times, preferably several, or even up to 10 times, the amount of alkali metal contained in the amalgam which is formed in the cell during the same unit of time. In effecting such circulation, the amalgam is passed in countercurrent flow to the reoxidized starting material issuing from the oxidation phase and flowing into a special reduction vessel.

The amalgam stream circulating through the reduction vessel may directly be produced at the corresponding high rate by the electrolytic cell, with the partially spent amalgam being recycled to the cell; but desirably, and particularly in connection with chlorine alkali electrolysis, an amalgam stream is withdrawn from the electrolytic cell and is circulated in a special cycle with increased rate through the reduction vessel. Then the partially spent amalgam is returned to the caustic reactor of the cell at a rate corresponding to the starting rate for makeup of consumed alkali metal. For obviating disturbances in the operation of the electrolytic cell, the partially spent amalgam is cycled back to the cell via a conventional caustic soda reactor, from which caustic is discharged and the purified mercury obtained is cycled back to the cell.

In Figure 3.1, apparatus for carrying out the process is illustrated to the extent necessary. Considering, first, the electrolytic cell used for producing the alkali amalgam, this is of conventional type, and for an illustration and description of its details reference is made to Industrial Electrochemistry, by C.L. Mantell, McGraw-Hill Book Co., New York, third edition, 1950, pages 397-411.

The cell body 1 is a gastight elongated housing with a bottom along which mercury flows to form the cathode of the electrical system. That flow is normally caused by providing a slight incline for the surface along which the mercury flows. In the present instance, mercury is shown as being introduced through the line 25 into the right hand end of the cell. Electric current applied to the cell body is thus transmitted to the mercury, which is generally referred to as the mobile mercury cathode. The other electrical contact, or anode, is in the form of a series of carbon plates spaced a small distance above the surface of the mercury. These plates are normally carried by suitable stems which pass out through gastight openings in the top of the cell. Also, the stems are insulated electrically from the cell. Suitable

FIGURE 3.1: PROCESS FOR THE CYCLIC OXIDATION AND REDUCTION OF HYDRAZOBENZENE



Source: R.M.R. Ornhjelm, U.S. Patent 2,992,071, July 11, 1961

means are provided for conducting electricity to the stems and thus through them to the plates.

For use in the electrical decomposition of an alkali solution, such as a brine made out of sodium chloride and water, provision is made for introducing the brine solution into the cell so that it will flow along on top of the mercury and at least fill the space between the upper surface of the mercury and the undersurface of the carbon anode plates. In Figure 3.1, the pipe 26 is provided for the introduction of such solution.

When the electric current is turned on, it passes between the anode and cathode through the brine solution decomposing the alkali chloride to produce chlorine gas and an amalgam of the alkali with the mercury. Spent brine solution collects on the top of the brine and can be readily removed. The chlorine gas is drawn off through the pipe 27, and the alkaline mercury amalgam passes off through the pipe 2.

It is also common practice to decompose the alkali mercury amalgam resulting from the operation of such cells, so that the pure mercury can be removed and recirculated to the cell for reuse. The element in which such decomposition is effected, normally referred to as a caustic reactor, is shown at 20. In the present instance, however, all, or a desired portion, of the amalgam produced by the cell is first to be employed for other purposes, so that instead of all of it being recirculated directly to the caustic reactor 20, all, or a desired portion, flows through the line 2 into the equalizing vessel 3 and then, by means of the pump 4, through the line 5 and into the reduction vessel 6. There, the amalgam loses some of its alkali metal so that as it is returned through the line 7 into the equalizing vessel 3 it is not of the original strength. However, amalgam from the equalizing vessel 3 is drawn off through the line 19 into the caustic reactor 20.

Alternatively, the cell may be of capacity to exceed the demands of the remainder of the system. In such case, flow through the line 2 can be adjusted by means of the valve 28 with part of the full strength amalgam being diverted through the line 29 to join with the line 19, and thereby flow directly into the caustic reactor without passing through the rest of the system. In either event – whether the amalgam be of full strength or have some of its alkali removed – it is broken down in the caustic reaction in the following manner. Water is introduced at the right hand end through the line 21 which reacts with the alkali in the amalgam to produce caustic, which is drawn off through the line 22. At the same time, hydrogen gas is liberated and is taken off through the line 30. Pure mercury remains, which is drawn off through the line 23 and pumped by the pump 24 through the line 25 back into the cell body 1.

The alkali amalgam produced by the cell contains from 0.1 to 0.3% alkali and, as already pointed out, is wholly or partly fed to the equalizing vessel 3. Here, this fresh amalgam will be mixed with amalgam of lower alkali content returned from the reduction vessel 6 through the line 7. This returned amalgam will have an alkali content of 0.01 to 0.2% alkali. The remainder of the alkali is that which has been used up in the reduction vessel 6 for the production of alkali peroxide.

The mixture of new amalgam and partially spent amalgam in the equalizing vessel 3 will, depending on circumstances, ideally form a mixture containing alkali of from 0.05 to 0.25%.

It is actually such a mixture which is fed to the reduction vessel 6 through the line 5 by means of the pump 4.

The important feature of the process is that on a flow basis the amount of amalgam mixture circulating in a unit of time from the equalizing vessel 3 through the reduction vessel 6 and back to the equalizing vessel through the line 5 and the pump 4, should be considerably greater than the amount of amalgam fed through the line 2 into the vessel 3 from the electrolytic cell 1. In fact, it may well be up to ten times greater. It is by this increase in flow rate without increase in overall volume of amalgam that the process enables the previously theoretical, or mere laboratory, system to be made operable with a capacity that makes it commercially acceptable.

A mixture fed back from the equalizing vessel 3 through the line 19 through the caustic reactor 20 has approximately the same content of alkali as the amalgam mixture which is fed through the line 5 into the reduction vessel 6. In quantity, however, the amount of amalgam passing through the line 19 is somewhat less than that introduced into the equalizing vessel through the line 3, the difference being consumed in the reduction vessel 6 and the amount of amalgam in the equalizing vessel 3 accordingly being less constant. By the inclusion of the equalizing feature in the process, however, it is apparent that it is possible to recirculate amalgam from and back to the equalizing vessel at a much greater rate than the rate at which full strength amalgam is produced by the cell 1.

Considering now the other features of the method generally previously known, the material being reduced by the amalgam in the reduction vessel is an azobenzene solution. This enters the vessel through the line 18 at its lower end and follows upwardly through the vessel 6 in countercurrent to the flow of the amalgam down through that vessel. It is thus reduced by the contact with the amalgam to the hydrazobenzene and flows off from the top of the vessel 6 into the oxidation vessel 9. There it is subject to oxidation by oxygen introduced through the line 10, while being stirred by means of the stirrer 12. Any excess oxygen is drawn off from the oxygen chamber 9 through the line 11 at the top of that chamber.

The azobenzene solution mixed with alkali peroxide brought off with the hydrazobenzene solution into the oxidation chamber 9 are passed via the line 13 at the bottom of the chamber 9 to the centrifuge 14. The centrifuge separates the peroxide from the azobenzene, and the peroxide is drawn off at 15. At the same time, the azobenzene solution drawn off at 16 and by the action of the pump 17 is forced through the line 18 back to the reduction vessel 6.

It is, of course, to be understood that the flow of the various streams can be controlled and that the process may also be performed batchwise as far as oxidation and reduction phases, as well as amalgam introduction, are concerned. The results obtained as compared to those obtained by prior methods without increased circulation rate will become evident from the following example.

In a reduction vessel 6, 50 mm. in diameter and 360 mm. high, filled with glass beads of 5.2 mm. ø, was introduced an alcoholic azobenzene solution with an azobenzene content of 20 g./l., at a rate of flow of 52 $cm.^3/min.$ and at a temperature of 60°C. in the reduction vessel. In countercurrent flow from the equalizing vessel was introduced amalgam with a Na content of 0.10% and at a rate of flow varying so that the amount of Na in the amalgam

flowing through the reduction vessel 6 per minute was in proportion to the Na amount contained in the amalgam formed in the electrolysis cell within the same period of time as shown in column I of the following table. Column II gives the reduction result as expressed in percentage of the azobenzene amount, and column III discloses the gram amount of produced peroxide expressed as $Na_2O_2.8H_2O$, all per minute.

I	II	III
	Percent	
0.5	30	0.41
1.0	50	0.70
2.7	65	0.90
5.0	80	1.10
8.0	97.5	1.34
10.0	98.5	1.36

A too strong alkalinity possibly occurring in the oxidation phase may be neutralized by an acidic additive, e.g., by adding hydrochloric acid which reacts to form sodium chloride which is recovered together with the peroxide.

It has also been ascertained that for obtaining the greatest possible reducing capacity, complete reduction of the oxidized hydrocarbon compound (commonly azobenzene) is not essential, but that reduction should be carried out to 98% at the highest, preferably to 80 to 85% only. In this way it is possible to prevent the azocompound from being converted into products which cannot be utilized in the production of peroxides.

In distinction from the first proposed methods, it has subsequently been suggested that the use of a benzene-alcohol mixture as a solvent, in place of using alcohol, would only be more advantageous for enhancing the solubility of an organic auto-oxidizable compound, e.g., azobenzene. Practice has shown, however, that in many respects it is more beneficial to use solely ethanol, e.g., raw sulfite alcohol. Then the concentration of the organic compound will remain low, in consequence of which the obtained peroxide will not become colored. Also attendant explosion hazard will diminish appreciably and operational safety will increase correspondingly. By using raw sulfite alcohol in place of the benzene-alcohol mixture, the equipment can be appreciably simplified; this naturally beneficially affects commercial realization of the process.

Moreover, it has been ascertained that the process can best be carried out at a temperature exceeding 35° C., preferably at a temperature range of from 65° to 79° C. For obtaining the greatest possible capacity, impure azocompounds, e.g., azobenzene should not be used. If technical materials are used which contain azo dyes and nitro compounds, the yield as calculated from the auto-oxidizable compound will decrease by 25 to 30% of that obtained on using a pure azo compound.

FILTERING OXYGEN-CONTAINING SOLUTION THROUGH NOVEL REDOX SYSTEM

Farbenfabriken Bayer AG; Maneck, G. (37): In this process it has been found that

hydrogen peroxide can be obtained in a simple, convenient and economic manner by filtering solutions containing oxygen through high molecular weight redox systems.

Suitable high molecular weight redox systems are polymerization resins or polycondensation resins having a redox system attached or incorporated by condensation or polymerization. Redox systems of this type for instance are all compounds having an orthoparaquinoidal structure, hydroxy compounds, enediol compounds, compounds containing SH groups, N-alkylated pyridine derivatives or leuco dyestuffs. Solvents which are suitable in the process are for instance water, hydrocarbons, halogenated hydrocarbons, alcohols, aldehydes, ketones, esters, organic phosphonates or mixtures of these. Besides, solvents may be used which have no dissolving power for hydrogen peroxide.

In a preferred embodiment of the process, the formation of hydrogen peroxide is favored by adding organic or inorganic stabilizers to the solutions containing oxygen. Stabilizers which are suitable for this purpose include sodium methaphosphate and 8-hydroxy quinoline, which are well-known in the literature. (See W. Machu, "Das Wasserstoffperoxyd und die Perverbindungen", Wien, Springer, Verlag, 2nd edition 1951, page 195 seq.) (75)

It is of advantage to conduct the process with solutions containing oxygen at a very high concentration. Solutions having an oxygen content as high as possible can be obtained, for instance, by saturating the solution with oxygen under pressure. When using solutions which are very rich in oxygen, it is preferable to carry out the process by filtering the solutions enriched with oxygen through the carriers of the redox systems which are incorporated in closed filters as they are used, for instance, in ion exchange processes.

In order to obtain hydrogen peroxide in very high yields, it is of advantage to carry out the process at low temperatures. Besides, it has proved to be of advantage to saturate once more the hydrogen peroxide solutions issuing from the filters with oxygen and to repass the solutions thus saturated through the redox systems. Before passing the solutions containing oxygen through the redox systems, it is necessary to convert the redox system into the reduced state. This can be accomplished by treating the system with reducing substances, for instance sodium dithionite, sodium sulfide, titanium trichloride or hydrogen.

As compared with prior art processes of producing hydrogen peroxide by means of dissolved redox systems, this process offers the considerable advantage that hydrogen peroxide solutions obtained can be used without any further processing operations. In contrast, the redox systems used in conventional processes must be separated from the peroxide solutions. Regeneration of the highly polymeric redox systems in this process is substantially more simple than the previously used redox systems. For the purpose of regeneration, the resins are treated with a reducing agent, whereupon the latter can be separated from the highly polymeric redox systems by merely washing. In the hitherto known processes, the dissolved redox systems must be regenerated in a separate processing step, generally by way of catalytic hydrogenation. For this purpose, the by-products formed in the production of hydrogen peroxide, such as ketones, acids, and aldehydes, must first be removed, since they contaminate the hydrogenation catalysts. Besides, the hydrogenation catalysts must be removed from the solutions after hydrogenation. Hence this process is substantially more convenient and economic than the prior art methods of producing hydrogen peroxide from solutions containing oxygen. The process is further illustrated by the following example.

A 5% titanium trichloride solution in 1 N sulfuric acid is filtered through a filter charged with 350 g. of an insoluble resin prepared from hydroquinone and formaldehyde according to the process described in German Patent 972,626, or according to other known processes (particle size 0.3 mm., mesh size 2.8 cm. diameter, charging height about 70 cm.). The redox exchanger is reduced during filtration. The reducing agent is separated by washing with a 1 N sulfuric acid which has been freed from oxygen by boiling. The sulfuric acid is then washed out with water which has been freed from oxygen by boiling. Removal of oxygen from the washing liquid can be promoted by blowing in nitrogen.

750 ml. of a 0.1% methaphosphate solution, which has been enriched with oxygen by passing through gaseous oxygen, is filtered through the column pretreated as described above. After recycling for 23 hours, a 0.023 N H_2O_2 solution has been formed. After another 72 hours, the concentration of the peroxide has been increased to 0.1 N. By continuing the recycling operation, the concentration can be increased up to 0.18 N. Subsequently, the column is exhausted and must be regenerated once more. The proportions of hydrogen peroxide in the solution can be further increased by saturating the solution again with oxygen and repumping the saturated solution over the reduced electron exchangers.

OXIDATION OF ISOPROPYL ALCOHOL

Shell Oil Co.; Mecorney, J.W., Gaertner, G.W., and Lehmann, A.S. (38): It is known that hydrogen peroxide can be manufactured by the oxidation of secondary alcohols. For example, if the alcohol is isopropyl alcohol, the process would be:

$$(CH_3)_2CHOH + O_2 \rightleftharpoons \underset{\text{acetone coproduct}}{(CH_3)_2CO} + H_2O_2$$

After distillation of the acetone and unreacted alcohol, H_2O_2 is concentrated. An 87% yield can be obtained in the process.

Notwithstanding the very satisfactory yield, this route to hydrogen peroxide has been found to suffer from two serious drawbacks. One is that the rate of production of hydrogen peroxide per unit volume of the reaction space is undesirably low. Therefore, for a reactor of any given size, the number of pounds of hydrogen peroxide that can be produced, for example per day, is limited to an undesirably low amount. With isopropyl alcohol, for example, the rates of production of hydrogen peroxide have been found to be limited to values on the order of only 5 to 10 pounds per day per cubic foot of reactor volume. This means that, for the production of hydrogen peroxide in quantities which would be of commercial interest, inordinately large equipment is required which adds greatly to the difficulty and cost of preparing hydrogen peroxide by this method.

A second difficulty, which is perhaps of even greater significance, is that the crude reaction product contains the hydrogen peroxide only in an undesirably low concentration. For example, an exhaustive study of the production of hydrogen peroxide by partial oxidation of isopropyl alcohol according to this known process has shown that the concentrations of hydrogen peroxide in the condensed reactor effluent are limited to concentrations below about

2.5 to 3.0% by weight. As a result, the process has required an undue amount of equipment for effecting the recovery of the relatively small concentrations of hydrogen peroxide which are contained in the crude reaction products. Furthermore, where, as would be likely, the unconsumed alcohol is to be recovered and recycled, an undesirably large amount of recycle is required for every pound of hydrogen peroxide produced.

The present process provides a new and improved method for the production of hydrogen peroxide by partial oxidation of primary and of secondary alcohols in the vapor phase. It provides for the production of hydrogen peroxide by the vapor phase partial oxidation of primary and secondary alcohols at rates, per unit volume of the reactor, which are increased by as much as 50-fold over the rates of production to which the above acknowledged known process appears to be limited. By means of the present process high concentrations of hydrogen peroxide are produced in the reactor effluent, materially above those obtainable by the known process. Recovery of hydrogen peroxide from the crude product is greatly facilitated by virtue of the increased concentrations of hydrogen peroxide.

In the present process, the oxidation of the primary or secondary alcohol is carried out in the vapor phase and at temperatures within the range of from about 350°C. to about 500°C. The alcohol is vaporized and the vapors, together with steam or other inert diluent if desired, are passed through a succession of oxidation stages or reaction zones under an essential superatmospheric pressure. In each oxidation state molecular oxygen, or a gas containing molecular oxygen, such as air or oxygen-enriched air, is introduced into and mixed with the vaporous mixture comprising the primary or secondary alcohol, by feeding a continuous stream of the molecular oxygen or O_2-containing gas into the stream of vaporous mixture passing into and through the stage.

After or concurrently with each of these incremental additions of molecular oxygen to the oxidation mixture, the oxidation reaction is caused to occur in each stage under the essential superatmospheric pressure, by appropriate control of the flow rates and by maintaining the temperature of the mixture at reaction temperature. After the last oxidation stage the mixture, which is formed by the successive partial oxidation of the alcohol, is withdrawn as effluent from the last oxidation stage; and the hydrogen peroxide is recovered from the withdrawn effluent.

For obtaining the advantages which are provided by the present process, it is essential to conduct the oxidation with the reacting vapors under superatmospheric pressure. Pressures not less than about 45 pounds per square inch (absolute) are employed. The pressure may range upwardly from 45 pounds per square inch (absolute) to about 1,000 pounds per square inch (absolute), although a preferred range is from about 60 pounds per square inch (absolute) to about 500 pounds per square inch (absolute). The pressure is applied by means which will be obvious, such as by forcing the respective feed streams into the reaction zones by mechanical pumps, and withdrawing the effluent from the terminal reaction stage through a pressure letdown device.

The staged oxidation of the primary or secondary alcohol is carried out with the alcohol present at all times in excess, on a molar basis, over the molecular oxygen in the reaction mixture. For obtaining high rates of production and high concentrations of hydrogen peroxide, while at the same time maintaining high yields of hydrogen peroxide based upon the

reactants consumed, it is necessary that both the relative overall amounts of alcohol and molecular oxygen fed to the system and the amount of molecular oxygen fed in each increment, or reaction stage, be controlled within limits. The overall ratio of primary or secondary alcohol to molecular oxygen should be maintained within the range of from about 2:1 to about 20:1 (mol basis) and preferably within the range of from about 5:1 to about 10:1.

In other words, for each mol of oxygen supplied to the total system, there should be supplied from about 2 to about 20, preferably from about 5 to about 10, mols of the alcohol. The amount of oxygen supplied to each of the successive stages should be between about 0.25 and 0.01, preferably between about 0.1 and about 0.04, mol per mol of alcohol in the reaction mixture at the point of addition and subject to the above limitation on the overall mol ratio.

In the simplest case one may employ a 2-stage addition of the oxygen. In this case, for example, about one-half of the total amount of oxygen may be preliminarily mixed with the vaporous primary or secondary alcohol and the mixture passed through a first oxidation stage. The remaining quantity of oxygen may then be introduced into and mixed with the mixture formed in the first oxidation stage, and the mixture thus formed passed through the second oxidation stage where the reaction is completed. The effluent from the second oxidation stage is collected and hydrogen peroxide is recovered from the collected effluent. Advantageously, more than two stages are employed, however, and the most desirable number of stages is from three to about eight, inclusive. The streams of gas containing molecular oxygen which are introduced into the respective stages ordinarily will contain approximately equal proportions of the total oxygen fed to the reaction system, although this relationship is subject to moderate variation.

It is essential that both alcohol and molecular oxygen be present together throughout the reaction zone during the staged addition of the oxygen and the subsequent reaction stages. In order to insure this, it is desirable to limit the total conversion of the oxygen fed to not over 90%. The amount of the alcohol present in each stage preferably is maintained between about 10 and about 500 mols per mol of oxygen by regulating the percentage conversion of the oxygen. The conversion of the oxygen fed into the reaction zone and the relative proportions of alcohol and oxygen in the reaction mixture may be controlled readily by regulation of the rates of feed to the reaction system and by the spacing of the inlets for the gas containing molecular oxygen. It is preferable, although not essential, that the residence time of the reaction mixture in the successive stages is progressively less from stage to stage in the direction of flow of the alcohol reactant. Total residence times of from about 1 second to about 1 minute are generally suitable.

The oxidation of the primary or secondary alcohol may be carried out in the presence of an inert diluent gas. The diluent conveniently may be steam, although nitrogen, helium, and other inert gases may be employed alone or in mixtures. For example, air may be employed as the gas containing molecular oxygen and, where the alcohol is one that forms an azeotropic mixture with water, the alcohol may be supplied in the form of the aqueous azeotrope. Ordinarily the dilution of the gas stream with inert diluents should be kept below about 50% and preferably to a minimum, since the principal consequence of the presence of a diluent gas is an increase in the volume of gas mixtures that must be handled. Equipment suitable for carrying out the process is shown diagrammatically in Figures 3.2a and 3.2b.

FIGURE 3.2a: SINGULAR TUBULAR REACTOR FOR THE MANUFACTURE OF HYDROGEN PEROXIDE BY OXIDATION OF ALCOHOLS

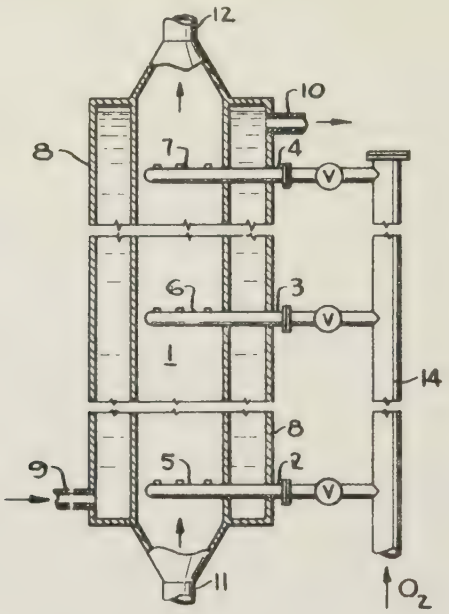
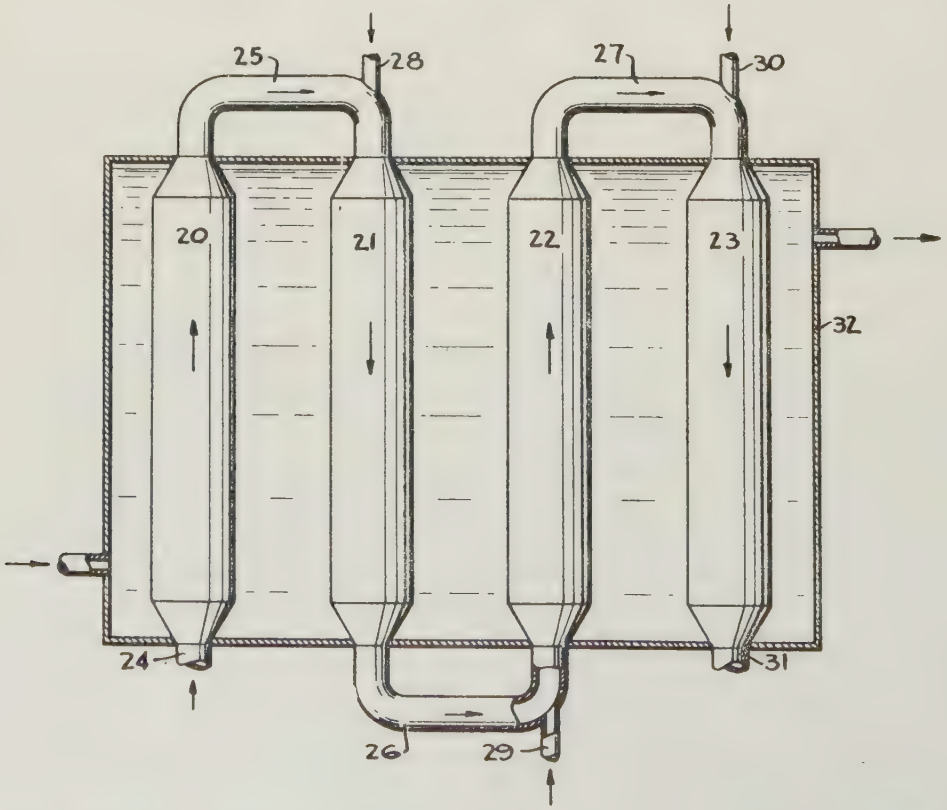


FIGURE 3.2b: PLURAL TUBULAR REACTORS FOR THE MANUFACTURE OF HYDROGEN PEROXIDE BY OXIDATION OF ALCOHOLS



Source: J.W. Mecorney, G.W. Gaertner, A.S. Lehmann, U.S. Patent 3,003,853, October 10, 1961

In Figure 3.2a is illustrated a single tubular reactor 1 with spaced oxygen inlets 2, 3, and 4 provided with manifolds 5, 6, and 7, respectively, or other gas dispersing means. The reaction tube is surrounded by jacket 8, through which a fluid heat exchange medium may be circulated by inlet 9 and outlet 10, or in place of the heat transfer system shown there may be employed a heater, such as electrically heated strips. The primary or secondary alcohol, after volatilization in a suitable vaporizer (not shown) is introduced via inlet 11 while separate streams of oxygen are introduced at inlets 2, 3, and 4 from conduit 14. Oxygen also may be mixed with the alcohol vapors to their introduction into the illustrated reactor by a suitable inlet (not shown) in feed line 11. Product gas is withdrawn via outlet 12 and is conveyed to a condenser, where it is cooled or is quenched with water for cooling and condensation to the liquid state and subsequent recovery of the hydrogen peroxide.

In Figure 3.2b is illustrated equipment embodying plural tubular reactors 20, 21, 22, and 23 arranged in series flow with inlet 24 provided for introduction of the alcohol feed, with connecting lines 25, 26, and 27, with inlets 28, 29 and 30 for introduction of molecular oxygen, air, or other gas containing molecular oxygen, and with effluent line 31. The several tubular reactors may be mounted together in a jacket 32 containing a fluid heat transfer medium, or they may be provided with individual and separately controllable heating means, as where it may be desired to maintain the temperatures in the different stages at different levels.

Instead of employing tubular reactors, there may be employed for the different stages reactors tending more or less to the spherical in form, so as to reduce the amount of surface that will be exposed to the vaporous reaction mixture in a reactor of any given volume, and the feed to each stage may be introduced more or less tangentially to the inner walls and the product gas withdrawn via an outline leading from a position more or less centrally located in the reaction space, thereby tending to minimize contact of the reacting mixture with the reactor walls. In any event, the reaction vessels, or at least their inner surfaces, should be constructed of materials which are not incompatible with hydrogen peroxide, such as glass, stainless steel, porcelain, aluminum, tin, or a resin. Feed lines and other conduits should be constructed with care to avoid possible contamination of the reaction vessels with materials which might favor decomposition of the hydrogen peroxide.

The hydrogen peroxide contained in the gaseous effluent from the terminal reaction stage may be recovered by any suitable method. One convenient method is to chill the gaseous effluent and then to distill the condensate, preferably in the presence of sufficient water and at subatmospheric pressures in order to minimize any likelihood of violent reaction between the hydrogen peroxide and the organic materials which necessarily are present. The alcohol which is not consumed may be recovered separately and recycled through the process with makeup feed. The carbonylic by-product (aldehyde or ketone) may be reduced, for example by hydrogenation, to convert it to the alcohol, and the alcohol thus regained may be recycled.

Hydrogen peroxide has been produced by this process at high rates of production, with high yields, based upon the alcohol and oxygen consumed, and with formation of a crude reaction product from which the hydrogen peroxide is easily recoverable by reason of the high concentration of hydrogen peroxide therein. In one run which is illustrative of those that have been performed, isopropyl alcohol was partially oxidized in the vapor phase at about 395°C.,

using an overall mol ratio of alcohol to oxygen of about 5:1 and operating at a pressure of about 60 pounds per square inch (absolute). The alcohol was vaporized and passed through a heated elongated reaction tube, the oxygen being introduced at points along the tube in a number of stages, the several streams of oxygen being about equal in volume.

The oxygen inlets were so spaced that the total residence time of the alcohol in the reactor (ca. 9 seconds), was about equally distributed among the several stages. Hydrogen peroxide was produced at a rate of about 70 pounds per day per cubic foot of the reactor, and the condensed effluent contained about 5 to 6% by weight of hydrogen peroxide. Under these same conditions, except that all of the oxygen is introduced with the alcohol feed, and atmospheric pressure is employed, the rate of production of hydrogen peroxide is only about 5 pounds per cubic foot of reactor volume per day and the concentration of hydrogen peroxide in the condensed reactor effluent is but about 2.5% to 3.0% by weight.

Isopropyl alcohol is particularly suitable as the alcohol reactant. However, the process can be applied to the production of hydrogen peroxide by vapor phase oxidation of other alcohols than isopropyl alcohol. Suitable other alcohols include primary alcohols, such as ethanol, propanol, butanol, isobutanol, and ethylene glycol, as well as secondary alcohols, such as s-butyl alcohol, s-amyl alcohol, cyclohexanol, and the like, and their homologs and analogs. Unsaturated alcohols, such as allyl alcohol and propargyl alcohol, likewise can be oxidized, although since they obviously are somewhat more valuable for other purposes than, for example, the saturated lower aliphatic primary and secondary alcohols, the latter generally are the ones that will be employed.

OXIDATION OF LOWER PARAFFINS

ICI Ltd.; Sampson, R.J. (39): The recovery in good yield of valuable intermediate products from rapid oxidation reactions of hydrocarbons with gases containing oxygen is complicated by difficulties in stopping the reaction at an intermediate stage, to prevent subsequent decomposition of these products. In particular, the preparation of such intermediate products as hydrogen peroxide and olefins by such a process from paraffin hydrocarbons having at least two carbon atoms is beset by difficulties which are, however, largely overcome by the present process. By intermediate products is meant products of a partial oxidation reaction, in which the reaction is stopped to prevent subsequent decomposition of these products as noted above.

Accordingly, the present process provides a method for the oxidation of a paraffin hydrocarbon with oxygen to form intermediate products in which the paraffin hydrocarbon and a gas containing oxygen are reacted together by mixing them to form a mixture above the upper explosive limit, and at a temperature of 400° to 600° C. for a short time, subsequently rapidly cooling the mixture by expansion to a temperature at which further reaction is substantially decreased.

The cooling of the products by expansion may be augmented by expansion into a cold gas; and/or the expanded gases may be further cooled at a slower rate to a temperature at which the products are sufficiently stable to permit their further treatment without substantial decomposition (for example in purification processes such as distillation). Cooling is preferably

effected by passing the gases from a high pressure zone to a low pressure zone through an orifice, such as a nozzle, so that cooling occurs by expansion in which the gas molecules acquire a more directed and less random movement. Either of these zones may be at atmospheric or other pressure.

In order to prevent loss of benefit, due to conversion of this directed movement into random movement by collision with vessel walls, a cooling gas or water spray may be introduced into the moving gas stream. The latter technique has the advantage that it may also serve to extract hydrogen peroxide from the reaction products, the resultant solution of hydrogen peroxide being further purified if necessary, for example to remove aldehydes which may be formed.

Suitable short contact times are 1 to 10 milliseconds or higher, the time selected being dependent upon the nature of the reaction. Preferably, however, the contact time does not substantially exceed 30 milliseconds. In general, shorter reaction times are required for higher reaction temperatures and pressures. These short contact times in which the reaction gases are mixed at 400° to 600°C. are preferably effected by mixing separate streams of the reactant gases previously heated sufficiently to give a mixture within the stipulated temperature range. The reactant gases are preferably mixed in one or more small bore mixing tubes in which the gases flow at turbulent rates to effect rapid mixing. The lower paraffins such as ethane and propane, with at least two carbon atoms, are preferred for use in the process.

Preferably the reactant gases are mixed in proportions of at least 5 volumes of paraffin per volume of oxygen. Although theoretical considerations suggest that optimum yields of hydrogen peroxide are provided by maximum oxygen partial pressures, when reacting paraffins higher than ethane, in fact to maintain the mixture above the upper explosive limit, the oxygen must be attenuated with another gas, which is preferably of simple molecular structure, for example monoatomic or diatomic, in order to obtain maximum cooling effect by expansion. The oxygen is therefore suitably attenuated with an inert elemental gas, for example nitrogen. Preferably, however, the oxygen is attenuated with a rare gas, particularly helium or argon, which gives a large cooling effect by expansion.

The reaction of the process is best carried out at a temperature between 500° to 600°C., and at moderately elevated pressures not in substantial excess of 20 atmospheres. The principal products from the process, using paraffins with at least two carbon atoms, are hydrogen peroxide and the corresponding olefins. They are obtained in good yields, although minor amounts of other products, such as epoxides and aldehydes, may also be produced. Hydrogen peroxide may be readily extracted from the gaseous reaction products by condensation.

The following is an example of operating the process. 400 liters per hour of ethane, preheated to approximately 600°C., were fed into a short fine bore capillary tube in which it was admixed in turbulent flow with 200 liters per hour of air fed at approximately the same temperature. The reactant gases were together in the capillary tube for approximately 0.2 millisecond, in which time they became thoroughly mixed. The capillary tube was arranged in a reaction zone maintained at 1.3 atmospheres pressure and at 600°C., by controlling the preheat temperature of the reactant gases. The products escaped from the reaction zone through a nozzle comprising an elongated capillary tube of 2 mm. bore which led to a

water-cooled liquid collection zone at atmospheric pressure. The residence time of the reactant gases in the reaction zone was approximately 30 milliseconds.

The liquid collected in the water-cooled zone consisted chiefly of hydrogen peroxide, corresponding to 3.4% conversion of the oxygen fed, and water. The product gases which remained uncondensed consisted chiefly of unchanged reactant gas and ethylene, corresponding to 5.5% conversion of the ethane in the reactant gases fed.

ESTERIFICATION OF ORGANIC PERACIDS

Wacker-Chemie GmbH; Lohringer, W. and Sixt, J. (40): It is known that organic peracids can be hydrolyzed with water in a reversible reaction to hydrogen peroxide and the corresponding organic acid. In the equilibrium, however, considerable quantities of peracid are present even in case of a larger water content, so that the yield of hydrogen peroxide is comparatively small. Besides, the quantity of the peracid is increased when the process is performed in the presence of saponification catalysts, such as sulfuric acid, especially when such solutions are distilled. Therefore, no hydrogen peroxide could be expected on the basis of these chemical conditions that would be free from any noxious organic peracid.

It has now been discovered that it is surprisingly easy, with a rapid reaction and excellent yield, to obtain hydrogen peroxide from organic peracids, such peroxide being free of troublesome peracid and/or organic acid with which the hydrogen peroxide could react mutually, if the peracid is converted with alcohol in the presence of an esterification catalyst at temperatures preferably below 100° C.; hydrogen peroxide and organic acylester are formed, and the hydrogen peroxide thus produced is separated from the organic ester. The use of peracetic acid and perpropionic acid is particularly advantageous. Besides other known esterification catalysts, sulfuric acid and cation exchangers are especially suitable. At the same time, during this reaction the corresponding nonperoxidized organic acids which are contained in the peracids, perhaps as a thinner, are also esterified.

In order to obtain pure hydrogen peroxide, the ester can be easily removed from the system. But the simplest way is to eliminate it by distillation after alcohols having 1 to 7 carbon atoms have been added, where due to the continuous removal of the troublesome organic acid component the equilibrium is shifted more and more toward the side of the hydrogen peroxide which is left as a residue.

Basically, aliphatic, cyclic and mixed aromatic alcohols can be used for the reaction. For the separation by distillation in the present process, alcohols with a low boiling point, such as methyl alcohol and ethyl alcohol, are useful. In order to esterify the peracid and also the acetic acid, for instance, a mixture of peracetic acid-glacial acetic acid of a quantity slightly more than the theoretical is mixed with methyl alcohol in the presence of about 2 to 6 parts by weight of concentrated sulfuric acid and/or phosphorous acid, or up to about 50 parts by weight cation exchanger, per 100 parts by weight of starting reactant materials and distilled.

During the reaction and also during the distillation, normal pressure or, if necessary, a slight vacuum can be applied. The formation of the ester and hydrogen peroxide begins at

once and methyl acetate begins to distill over. The transformation can be described by the equation:

$$CH_3COOOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O_2$$

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

Here it remains uncertain whether acetic acid is formed as an intermediate by hydrolysis from peracid. The transformation into methyl acetate is practically quantitative. Distillation is continued until all the ester has gone over, which can be noticed by the rising temperature.

The distillation residue contains the hydrogen peroxide formed in an equivalent quantity in mixture with water. The former derives from the peracid, the latter from the acetic acid of the mixture which is also present. The residue also contains the added esterification catalyst and perhaps small quantities of alcohol. It is not necessary to add water in order to set off the esterification reaction.

If the content of organic acid is larger, naturally more water is formed. At any rate, a comparatively concentrated aqueous hydrogen peroxide solution remains in the residue. Consequently, a hydrogen peroxide solution containing very little water can be obtained from peracid-carboxylic acid mixtures with high peracid concentration, perhaps diluted with inert solvents. In order to avoid an explosion, however, H_2O can be added when distilling off the excess alcohol.

Instead of separating the ester by separate batch distillation methods, a continuous distillation method can be used, for instance by running in the reaction fluid at an appropriate section of the column while piping off the ester at the head of the column and taking off the hydrogen peroxide solution at the lower end. The separation of the aqueous hydrogen peroxide solution can further be made possible by aiding the formation of an ester layer after perhaps adding ligroin or petrol ether and possibly water.

The further treatment of the hydrogen peroxide solution for the purpose of separating the catalyst and the alcohol which may still be present, can be done by distillation as well as filtration, or in any other suitable way. The ester obtained in each case can either be used as a solvent or split up into its natural components, namely organic acid and alcohol. In the latter case, the alcohol as well as the recovered esterification catalyst can be recycled into the process.

The following may serve as an example to illustrate the process. 36 parts by weight of a mixture of peracetic acid and glacial acetic acid, with the mixture containing 42.6% by weight of peracid, are mixed with 30 parts by weight of methanol and 2.5 parts of concentrated sulfuric acid under cooling, and subsequently warmed up to 60°C. and subjected to fractional distillation under normal pressure, until methyl acetate, which goes over at 53°C. is entirely driven off. A small part of the methanol which did not go over with the methyl acetate is subsequently separated by fractional distillation from the residue under a slight

vacuum. The result is a hydrogen peroxide solution which is practically free of peracetic acid and acetic acid and contains 45% by weight of hydrogen peroxide. There is no loss of active oxygen with this operation.

OXIDATION OF ALKALI METAL AMALGAM

The Dow Chemical Co.; Long, R.S., and Noma, A.T. (41): The oxidation of alkali metal amalgams, particularly sodium and potassium amalgam, to the corresponding alkali metal peroxide is understood in the art. However, until now recovery of the alkali metal peroxide values as hydrogen peroxide by direct extraction of the oxidized amalgam with aqueous acid has not been successful, primarily because of the instability of the hydrogen peroxide in aqueous acid in the presence of coextracted heavy metal cations.

The present process comprises treating sodium or potassium peroxide, prepared by direct oxidation of the corresponding amalgam, with a mineral acid carried in an organic solvent, thereby to convert the alkali metal peroxide into hydrogen peroxide, and at the same time preferentially extracting the hydrogen peroxide into the organic phase. The hydrogen peroxide product can be recovered from the organic extract by water stripping or other separation techniques.

More particularly, sodium or potassium peroxide is produced by contacting the corresponding amalgam, containing as a maximum about 0.2 weight percent of the alkali metal with substantially dry air, oxygen or mixtures of these gases at a temperature below about 60° C. for a maximum period of about 5 minutes. Preferably, sodium amalgam is employed.

The oxidized amalgam, having the sodium or potassium peroxide in the presence of excess mercury, is extracted with a mineral acid, preferably phosphoric, hydrochloric, sulfuric acid or mixtures of these acids carried in an aliphatic alcohol, having from 1 to about 6 carbon atoms, aliphatic carboxylic esters having from about 2 to about 4 carbon atoms, aliphatic ketones having from 1 to about 4 carbon atoms, trialkyl phosphates in which each of the alkyl groups has from about 4 to about 8 carbon atoms, or di- and trialkyl amines in which each of the alkyl groups has from about 8 to about 12 carbon atoms.

Particularly suitable organic solvents for use as a carrier for the mineral acid and H_2O_2 extractant in the present improved process are n-butanol, methyl isobutyl ketone, n-butyl acetate, ethyl acetate, tributyl phosphate, trioctyl phosphate, isoamyl alcohol, isobutyl alcohol, tetrabromoethane, triisooctyl amine and didodecyl amine.

Preferably, substantially water-immiscible organic liquids, e.g., the trialkyl phosphates, will be employed as solvent for the mineral acid to facilitate subsequent recovery of the hydrogen peroxide product by water stripping. The use of the acid-organic liquid extractant provides for conversion of the alkali metal peroxide into hydrogen peroxide in good yield, as well as giving simultaneous extraction of the hydrogen peroxide into the organic phase without detrimental product decomposition.

As already stated, the extracted hydrogen peroxide is recoverable from the organic extract by water stripping or other separation techniques. Water stripping is particularly effective

for those organic liquids which are essentially water-immiscible or only slightly miscible with water. With these substances ordinarily the amount of water for stripping ranges from about 0.2 to about 5 times that of the organic phase.

The concentration of acid to be employed in the organic extract ranges from about 5 to about 70 weight percent. The actual concentration for optimum hydrogen peroxide conversion and recovery is readily determined for any particular organic solvent-mineral acid solution employed.

The amount of the acid-organic liquid extractant to be employed is not critical, although ordinarily an amount of solution sufficient to provide at least enough acid to convert substantially all of the alkali metal peroxide to hydrogen peroxide is used. Preferably, an amount of organic solution to provide an excess of the acid component over that required for H_2O_2 production is employed. Large excesses of the conversion-extractant solution usually are not used, because of the inconvenience in handling large volumes of liquid and the subsequent stripping of hydrogen peroxide from them.

The treatment of the oxidized amalgam by the acidic organic extractant can be carried out in continuous, cyclic or batch-type operations. The following example will serve to further illustrate the process.

A dry, medium porosity sintered glass funnel about 5 3/4 inches high and having a 1 3/4 inch inside diameter was fitted with a No. 10 rubber stopper which had been bored to receive a gas outlet tube. The funnel was connected at the stem through a flow meter and a calcium chloride drier to an oxygen cylinder. The funnel was unstoppered, charged with about 295.6 grams of a substantially dry sodium amalgam (0.043 weight percent sodium) and restoppered. Oxygen gas at about 10 pounds per square inch gauge pressure and about room temperature, i.e., from about 18° to about 25°C., was bubbled through the amalgam with swirling for about 3 minutes, at a flow rate of about 4,500 cubic centimeters per minute. During this early part of the reaction period, the mass foamed. By the end of the 3 minutes time period, the foaming essentially had ceased and the oxidized amalgam began to "peel" away from the funnel wall. The resulting oxidized amalgam was agitated for several minutes with about 20 milliliters of a solution of sulfuric acid in tributyl phosphate.

Two-phase titration of an aliquot of the resulting tributyl phosphate extract with thiosulfate showed conversion of sodium peroxide into hydrogen peroxide and extraction of the hydrogen peroxide into the tributyl phosphate in a yield of about 71.8% based on the sodium content of the amalgam.

The acidic tributyl phosphate reactant-extractant solution was prepared by contacting for several minutes about equal volumes of tributyl phosphate and aqueous sulfuric acid solution containing about 32% by weight H_2SO_4. This action gave extraction of H_2SO_4 into the alkyl phosphate, after which the resulting acid-containing organic solution was separated from the H_2SO_4-depleted residual aqueous mass.

FROM ALKALI METAL PEROXIDE IN A CYCLIC PROCESS BY REACTION WITH AN ORGANIC ACID

Canadian Industries Ltd.; Archambault, J.O., and Lusby, G.R. (42): In Canadian Patent 673,355 issued on October 29, 1963, is disclosed a process for the manufacture of hydrogen peroxide by the reduction of the disodium salt of an anthraquinone disulfonic acid with hydrogen sulfide and subsequent oxidation of the reduced product with oxygen. The resulting hydrogen peroxide is separated from the alkaline disodium anthraquinone disulfonate solution by precipitation as calcium peroxide by the addition of calcium hydroxide at room temperature. The calcium peroxide product is separated from the aqueous solution of anthraquinone disulfonic acid salt and is subsequently converted to hydrogen peroxide by known methods, such as that described in U.S. Patent 2,695,217.

However, the known methods of converting calcium peroxide to hydrogen peroxide yield a solution or slurry of the calcium salt containing hydrogen peroxide from which the hydrogen peroxide must be separated. The elimination of the separation process, therefore, would simplify the recovery of the hydrogen peroxide from the reaction mixture. Likewise, in the process for the production of hydrogen peroxide by the reaction of barium peroxide with an acid, the hydrogen peroxide product must be separated from the barium salt.

It is an object of the present process to provide a method for the manufacture of hydrogen peroxide in which an alkaline earth metal peroxide product is efficiently converted to hydrogen peroxide. Another object is to provide a liquid-liquid extraction process for the recovery of hydrogen peroxide from alkaline earth metal peroxides.

The process comprises contacting an aqueous slurry of an alkaline earth metal peroxide with a water-insoluble organic acid dissolved in a water-immiscible solvent, whereby the metal peroxide reacts with the organic acid to form an aqueous solution of hydrogen peroxide and a metal salt of the organic acid which is soluble in the water-immiscible solvent; separating the aqueous solution from the water-immiscible solution; treating the water-immiscible solution of the metal salt of the organic acid with an aqueous solution of an inorganic acid, thereby regenerating the organic acid; and separating the metal in the form of a salt of the inorganic acid from the water-immiscible solvent, the regenerated solution of the organic acid being then employed for the extraction of further portions of the aqueous slurry of alkaline earth metal peroxide. It has been found that the alkaline earth metal salt of the inorganic acid is either soluble or dispersible in the aqueous phase and therefore can readily be separated from the water-immiscible solvent.

It is envisaged as a modification of this process that the solution of the alkaline earth metal salt of the organic acid dissolved in a water-immiscible solvent be extracted with water to remove residual hydrogen peroxide carried over into the water-immiscible solvent. The aqueous solution of hydrogen peroxide thus obtained may be added to the aqueous solution of hydrogen peroxide obtained by the primary separation.

The organic acids suitable for employment in the process include those branched chain organic acids containing at least 8 carbon atoms and which are substantially water-insoluble, but are soluble in water-immiscible solvents. It has been found that suitable organic acids are naphthenic acid, di(2-ethylhexyl) phosphoric acid, 2-ethylhexanonic acid and tertiary

monocarboxylic acids with 9 to 11 carbon atoms in the main chain, known as Versatic 911. The water-immiscible solvents suitable for use in the process are aromatic and aliphatic hydrocarbons which do not react with peroxide and which have serviceable viscosity and volatility at room temperature. Examples are xylene, toluene, n-hexane, cyclohexane and kerosene.

Water-soluble acids suitable for regeneration of the water-immiscible organic acid include sulfuric acid, sulfurous acid, phosphoric acid, hydrochloric acid and nitric acid. It has been found that carbon dioxide may be employed to regenerate 2-ethylhexanoic acid and tertiary monocarboxylic acids containing 9 to 11 carbon atoms in the main chain. Regeneration with carbon dioxide has commercial attraction in the case of the latter carboxylic acid since a cyclic process is possible, the by-product calcium carbonate being calcined to form dilute carbon dioxide (ca. 30%) which can be used again for conversion of additional portions of the calcium salt of the carboxylic acid.

The process may be carried out with any of the known apparatus which can be used for liquid-liquid extraction. Equipment may be of the type used for continuous countercurrent extraction, or it may be mixing-settling tanks.

More particularly, in the preferred embodiment of this process, the calcium peroxide slurry which normally contains small amounts of the sodium salt of an anthraquinone disulfonic acid is extracted with a solution of the organic acid (10% to 50% by weight) in a water-immiscible solvent. The distribution coefficients of hydrogen peroxide and the organic acid calcium salt between the organic and aqueous phases are such that the majority of the hydrogen peroxide will remain in the aqueous phase and the organic salt will remain in the water-immiscible phase. The two phases are then separated.

The hydrogen peroxide remaining in the organic phase can be extracted with a water wash. The calcium salt of the organic acid dissolved in the water-immiscible solvent is then treated with an aqueous solution of an inorganic acid, such as phosphoric acid. In this manner, the organic acid is regenerated and the calcium salt of the water-soluble acid is formed. The distribution coefficients between the organic and aqueous phases are such that the organic acid remains in the water-immiscible solvent. The calcium salt of the inorganic acid remains dissolved or dispersed in the aqueous phase. After separation of the two phases, the organic acid can then be used for the treatment of the next portion of calcium peroxide.

In comparison to the usually employed processes for the recovery of hydrogen peroxide from calcium peroxide, the liquid-liquid extraction procedure provides a much higher concentration of hydrogen peroxide in aqueous solution. For example, using calcium peroxide octahydrate, aqueous solutions containing 15 to 17% hydrogen peroxide can be obtained. In normally employed processes, the concentration of hydrogen peroxide is likely to be less than 5%. The process is additionally illustrated by the following examples.

A series of experiments was carried out in which hydrogen peroxide was recovered from calcium peroxide employing solutions of 2-ethylhexanoic acid in xylene. The solutions contained 2-ethylhexanoic acid in concentrations in the range from 10 to 33% by weight. The calcium peroxide was employed as calcium peroxide octahydrate, calcium peroxide dihydrate and an aqueous slurry of anhydrous calcium peroxide (ratio of CaO_2/H_2O being 2/1). The calcium

peroxide was agitated at room temperature with xylene/acid solution, and the xylene solution was removed by decantation. The decanted xylene solution was then extracted with water to remove dissolved hydrogen peroxide. The percentage of hydrogen peroxide in both of the aqueous solutions was determined. The results of the experiments are shown in Table 3.1. It can be seen that if the organic phase is extracted with water after separation from the aqueous phase, effective conversion of calcium peroxide to hydrogen peroxide is attained.

TABLE 3.1: EXPERIMENTAL RESULTS

Ex.	Solvent, Percent ethyl-hexanoic acid in xylene	Feed-Solid component of aqueous phase	Ratio Solvent to Feed	Percent H_2O_2 in aqueous phase	Percent H_2O_2 recovered in aqueous phase	Percent H_2O_2 recovered from organic phase	Total recovery, Percent
1	10	$CaO_2 \cdot 8H_2O$	100/6	20.0	71.0	22	93
2	10	$CaO_2 \cdot 2H_2O$	100/3				74
3	10	CaO_2	100/2	21.0	39	39	78
4	20	$CaO_2 \cdot 8H_2O$	100/11	15.6	77.7	16.3	94
5	20	$CaO_2 \cdot 2H_2O$	100/4.8	42.8	47.7	50.8	98.5
6	20	CaO_2	710/28	24.6	79	23	102
7	20	$CaO_2 \cdot 2H_2O$	925/65	30.5	57	28	85
8	25	$CaO_2 \cdot 8H_2O$	100/15	16.7	80.1	21.8	101.9
9	25	$CaO_2 \cdot 8H_2O$	100/15	17.1	87.4	16.4	103.8
10	25	$CaO_2 \cdot 8H_2O$	300/45	14.6	83		
11	25	CaO_2	1,000/50	35.1	37.4	51.5	88.9
12	25	CaO_2	175/7.5	27.6	58.3	29.4	87.7
13	25	CaO_2	415/16.5	28.8	55.5	32.2	87.5
14	33	$CaO_2 \cdot 8H_2O$	100/20	16.9	79.1	21.7	100.8

HYDROLYSIS OF PERACETIC ACID BY PASSING AN AQUEOUS STREAM OF THE LATTER THROUGH A BED OF CATION-EXCHANGE RESIN CATALYST

Celanese Corp.; MacLean, A.F., and Stautzenberger, A.L. (43): In this process, hydrogen peroxide is produced by bringing a mixture of water and peracetic acid into contact with a strong acid catalyst (of ionization constant above 0.01), desirably an insoluble acid catalyst, to effect the reaction of the water and peracetic acid and form hydrogen peroxide and acetic acid, and then separating the catalyst from the reacted mixture. Preferably, the process is carried out by passing a stream of aqueous peracetic acid continuously through a bed of a cation-exchange resin, after which the reaction mixture is treated to separate the aqueous hydrogen peroxide from the acetic acid formed in the reaction and from unreacted peracetic acid. The peracetic acid is conveniently obtained by the process described in U.S. Patent 3,192,256.

As stated, an acidic cation-exchange resin may be employed as a catalyst for the reaction of the water and peracetic acid. This resin is advantageously a strongly acidic resin, e.g., a resin having free sulfonic acid groups, particularly a sulfonated cross-linked resin such as the resins of U.S. Patent 2,366,007, e.g., the sulfonated styrene-divinyl benzene copolymers. Other suitable cation-exchange resins are, for example, the phenol sulfonic acid-formaldehyde reaction products. It is desirable, of course, that the resin be substantially free of heavy metal ions and similar materials which catalyze decomposition of peroxides. It is also desirable to include in the reaction mixture a minor proportion of a stabilizer against such decomposition, e.g., a sequestering agent such as sodium pyrophosphate,

dipicolinic acid or ethylene diamine tetracetic acid. The aqueous peracetic acid brought into contact with the acid catalyst preferably contains about 20 to 40% peracetic acid. It also contains a minor proportion, relative to the peracetic acid, of acetic acid.

In one convenient process, a stream of the aqueous peracetic acid is passed through a bed, desirably a fixed bed, of the acidic resin. The temperature of the bed may be, for example, in the range of about 10° to 90°C. The residence time of the reaction mixture in the bed is desirably such that about 50 to 80% of the peracetic acid is reacted. The reacted mixture leaving the bed of catalyst contains hydrogen peroxide, acetic acid, water and unreacted peracetic acid.

It has been discovered that water and peracetic acid form an azeotrope, which can be distilled from hydrogen peroxide, water and acetic acid. At atmospheric pressure (760 mm.), this azeotrope boils at about 95.5°C. and contains about 60% (26 mol percent) peracetic acid. This discovery is utilized in the isolation of aqueous hydrogen peroxide from the other components of the mixture leaving the bed of catalyst. Thus, the mixture may be subject to two distillations: in one distillation an azeotrope of water and peracetic acid is taken off overhead for recycling to the bed of cation-exchange resin; while in the other distillation the acetic acid is stripped off by the injection of an inert gas, which may be nitrogen, for example, but is most preferably steam. The residue from the two distillations is an aqueous solution of hydrogen peroxide.

The stripping of the acetic acid may be the first distillation in this sequence, but best results are obtained when the azeotrope distillation is carried out first. The two distillations are preferably effected in conventional distillation columns. Thus, in one embodiment, the stream of reacted mixture leaving the resin bed is fed to an intermediate portion of a fractionating column (subsequently termed an "azeotrope column"), and vapors of the peracetic acid-water azeotrope are taken off overhead. The stream of liquid mixture of water, hydrogen peroxide and acetic acid (containing for example, about 5 to 30% hydrogen peroxide, 5 to 30% water and the balance acetic acid) from the bottom of this azeotrope column is then introduced into the intermediate portion of a second fractionating column.

A stream of steam (e.g., about 1.5 to 10 parts of superheated steam per part of the residue from the azeotrope column) is fed at a lower point on the second column, aqueous acetic acid is taken off overhead, and aqueous hydrogen peroxide (containing, for example, about 10 to 35% hydrogen peroxide) is removed continuously from the bottom of the second column.

To minimize decomposition in the distillation columns used for separating the components of the aqueous reacted mixture, these columns may be operated at subatmospheric pressure. For example, the azeotrope column may be operated at a pressure of 93 mm. of mercury absolute, at which the boiling point of the peracetic acid-water azeotrope is about 47.5°C.; about one-half of the azeotrope formed under these conditions is peracetic acid.

Instead of employing a reduced pressure, a water-immiscible solvent which forms a three-component solvent-peracetic acid-water azeotrope of lower boiling point than the peracetic acid-water azeotrope, may be added to the top of the azeotrope column. In this case vapors of the three-component azeotrope are taken overhead, the vapors are condensed to form a two-phase mixture, most of the peracetic acid being in the aqueous phase, and the

water-immiscible phase is returned to the top of the azeotrope column. The amount of water-immiscible solvent supplied to the top of the azeotrope column is preferably just sufficient to cause formation of the desired azeotrope.

Preferably, the solvent is so chosen that the amount of peracetic acid in the aqueous phase is at least equal to half the amount of water in this phase. Thus, when n-heptane, which is the preferred solvent, is employed, the ternary azeotrope, formed at an overhead temperature of 77° to 78°C. at 760 mm. Hg, contains about 9% peracetic acid, about 77% heptane and about 14% water, and the peracetic acid content of the heptane phase is about 0.2 to 0.3%. Other solvents are benzene, hexane, octane, ethylene chloride, propylene chloride.

The acetic acid stripping operation is carried out at such a temperature as to maintain the stripping agent in gaseous form and to volatilize the acetic acid. Thus, when steam is the stripping agent the temperature should be at least 100°C. at atmospheric pressure.

In Figure 3.3, vapors of a mixture of peracetic acid and acetaldehyde from a reactor are fed through a line 11 to an acetaldehyde separation column 12 to which a solvent is supplied through a line 13. Acetaldehyde vapors are taken off overhead, with refluxing, through a line 14, and a solution of peracetic acid in the solvent is discharged below through a line 16. Water is added, through a line 17, to this solution and the resulting aqueous mixture is fed to a solvent removal column 18, from which vapors of solvent are taken off overhead and then condensed, for return through line 13 to the acetaldehyde separation column 12.

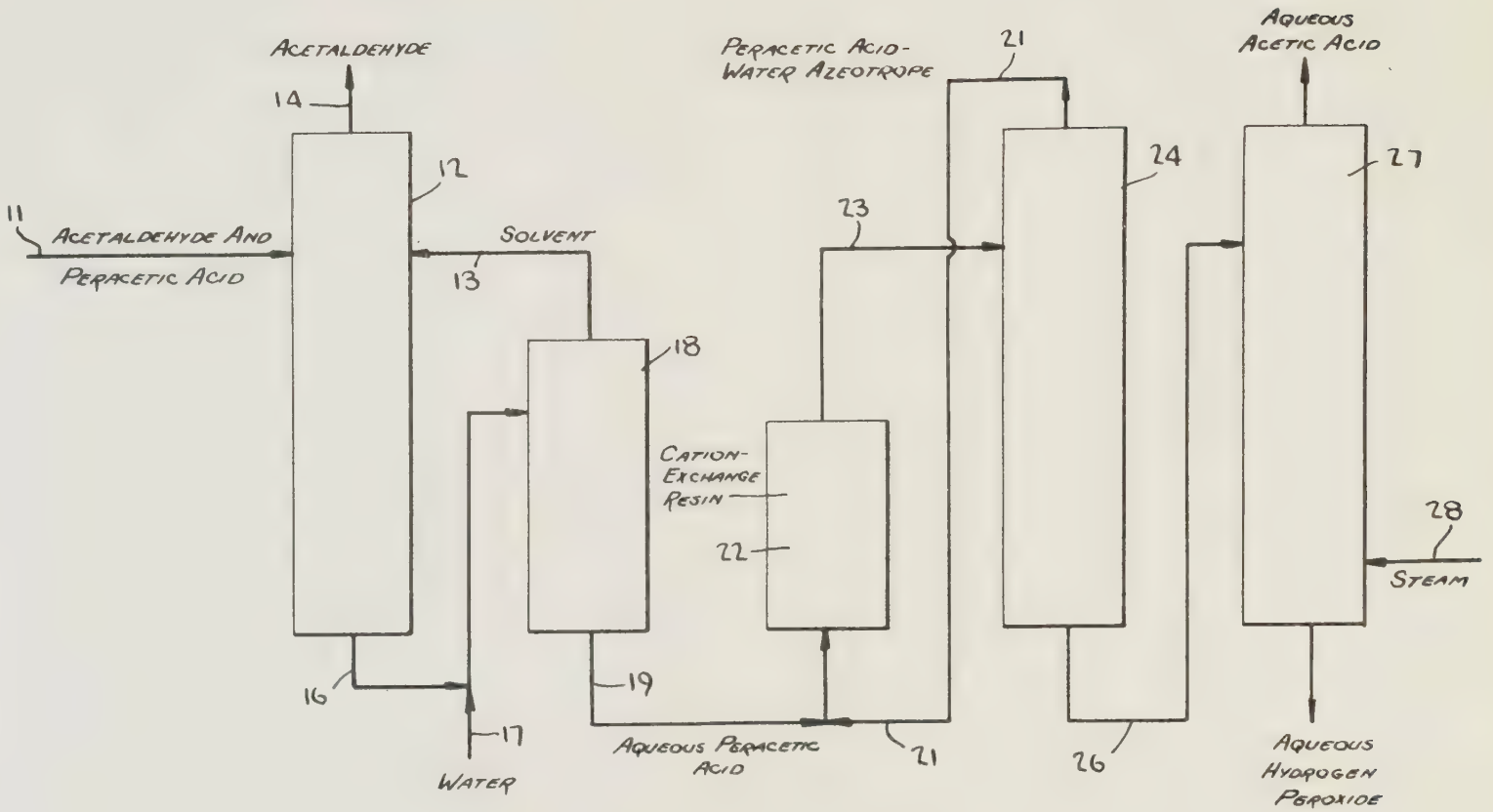
A solution of peracetic acid in water leaves the bottom of the solvent-removal column 18 through a line 19, is combined with recycled peracetic acid-water azeotrope from a line 21, and passes upward through a bed of granules of acidic resin contained in a reactor 22. The mixture then passes, through a line 23, to an azeotrope column 24, from which an azeotrope of water and peracetic acid is taken overhead, preferably with refluxing, through the line 21, this azeotrope being condensed and then recycled to the reactor 22.

The residue of water, hydrogen peroxide and acetic acid, from the bottom of the azeotrope column 24, is fed through a line 26 to an acetic acid stripping column 27, to which steam is supplied through a line 38, and from which aqueous acetic acid is taken overhead (desirably with just sufficient refluxing to avoid loss of hydrogen peroxide overhead), through a line 29. The residue from the column 26 is the desired substantially pure aqueous hydrogen peroxide solution. The following example is given to illustrate the process further.

The apparatus described in Figure 3.3 is employed. A stream of vapors containing 79% acetaldehyde and 18% peracetic acid, at a temperature of 140°C., is fed at the rate of 28,600 parts per hour through the line 11, into a 35-tray column 12 at 15th tray from the top, and methylal is fed through the line 13, at the 13th tray from the top, at the rate of 11,400 parts per hour. The column 12 is operated at a base temperature of 77°C. and a top temperature of 20°C., a pressure of 1,000 mm. Hg absolute, and a reflux ratio of 2:1. The water is supplied through line 17 at the rate of 5,200 parts per hour.

The column 18 has 100 trays and is operated at a base temperature of 100°C. and a top temperature of 42°C., at atmospheric pressure and at a reflux ratio of 0.8:1. The combined feed of water and methylal solution of peracetic acid is fed in at the 10th tray from the top

FIGURE 3.3: HYDROGEN PEROXIDE PRODUCTION BY HYDROLYSIS OF PERACETIC ACID



Source: A.F. MacLean, A.L. Stautzenberger, U.S. Patent 3,341,297, September 12, 1967

of column 18. The reactor 22 is filled with granules of Amberlite IR-120 (H) AG and is operated at a temperature of 42° C., the space velocity of the liquid through the reactor being 0.051 per minute.

The azeotrope column 24 has 25 trays, and the reacted mixture enters this column at the 12th tray from the top; the top temperature of this column is 78° C. and its bottom temperature is 100° C. The column is operated under a pressure of 450 mm. Hg absolute and a reflux ratio of 5:1.

The acetic acid stripping column 27 has 40 trays; the acetic acid-hydrogen peroxide-water mixture enters at the 3rd tray from the top; the steam at a temperature of 100° C. is introduced at the 39th tray from the top at the rate of 15,980 parts per hour; and the top and bottom temperatures in this column are 58° and 85° C. respectively. The pressure in this column is 100 mm. Hg absolute, and the column is operated at 1:5 reflux ratio. The residue from column 27 contains 35% hydrogen peroxide and 0.22% acetic acid.

SYNTHESIS IN HIGH YIELD FROM THE ELEMENTS IN LIQUID MEDIUM IN PRESENCE OF CATALYST

ICI Ltd.; Hooper, G.W. (45): Up to the present time, hydrogen peroxide has been produced industrially mainly by processes which involve either anthraquinones from which the separation of hydrogen peroxide is tedious, or else by electrolysis of ammonium bisulfate between platinum electrodes, which process is expensive. It has also been proposed to produce hydrogen peroxide by the direct union of hydrogen and oxygen, but no efficient process of this type has so far been devised. A new and advantageous process has now been developed, by which hydrogen peroxide can be made in considerably higher yield by contacting hydrogen and oxygen with a suitable solid catalyst in a liquid medium in the presence of water, an acid and a nonacidic oxygen-containing organic compound.

By nonacidic is meant not more acidic than water. Thus the nonacidic oxygen-containing organic compounds which may be used are alcohols, aldehydes, ketones, ethers, esters, amides and oxygen-containing amines. Carboxylic acids, on the other hand, are of limited effectiveness in fulfilling the function of the oxygen-containing organic compound and are excluded from the scope of the process.

In one preferred embodiment of the process, the acid is at least as strong as acetic acid and is more preferably an acid having an inorganic acidic radical. Conveniently there is used one or more of the following: sulfuric acid, nitric acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid, phosphoric acid and sulfonic acids. Of these acids, hydrochloric acid and sulfuric acid give especially favorable results. In another preferred embodiment, the acid is one whose anion has catalyst poisoning properties: as examples of such acids may be mentioned hydrogen sulfide and hydrogen cyanide. Mixtures of acids containing more than one from each of the above embodiments or of acids from both embodiments may be used. The acid concentration is preferably in the range 0.01 N to 2 N.

In addition to the acid, there is preferably present also one or more second acid radicals selected from the following list: sulfate, nitrate, fluoride, chloride, bromide, cyanide,

cyanate, thiocyanate and phosphate. The concentration of such acid radicals may be the same as that of the above mentioned acids. Preferably there is present at least one of the above radicals, which are halogen or pseudo-halogen acid radicals, especially chloride, to the extent of at least 10^{-5} N, especially in the range 10^{-4} N to 0.1 N. Concentrations above 0.1 N may be used, for example N, but no advantage is obtained thereby as a rule. It is possible to have present, in addition to the acid, a salt which provides the required second acid radical.

As preferred classes of nonacidic oxygen-containing organic compounds, may be mentioned alcohols and ketones, especially those having a solubility in water of at least 1% at room temperature, that is, alcohols and ketones containing up to about 8 carbon atoms per oxygen atom. Thus, the lower aliphatic mono-alcohols containing up to 8 carbon atoms may be used, and more especially those having up to 4 carbon atoms which are miscible with water at room temperature. Similarly, the lower aliphatic ketones containing up to 8 carbon atoms may be used, more especially acetone, methyl ethyl ketone and cyclopentanone. Acetone produces especially good results.

These organic compounds are preferably used in solution in the aqueous acid solution; and in order to enhance solubility, more than one of them may be present if desired. If, however, the solubility of a particular compound is low and is not sufficiently increased by the presence of another oxygen-containing compound, then that compound is preferably emulsified. If the oxygen-containing organic compound is basic, then the amount of acid present must of course be more than equivalent to the amount of base.

The proportion of nonacidic oxygen-containing organic compound to water is preferably more than 20:80, and especially from 40:60 to 90:10 by volume. It is believed that the acid, the organic oxygen-containing compounds and the second acid radical each function by deactivating those centers in the catalyst which promote the decomposition of hydrogen peroxide. The nonacid organic oxygen-containing compound also accelerates the formation of hydrogen peroxide.

The solid catalysts in the process preferably contain as metallic component at least one element from Group I or Group VIII of the Periodic Table. Of these metals, gold, platinum and palladium appear to be best. Palladium is especially effective.

Conveniently, the metallic component of the catalyst is palladium, either alone or alloyed or mixed with a minor proportion of one or more other metals, especially gold or platinum. The pure metal or metal mixture may be used in colloidal form if desired, but preferably is supported on a carrier, preferably forming 1 to 10% of the total catalyst by weight. The carrier may, for example, be a refractory oxide such as alumina (for example active gamma alumina), silica, silica-alumina, titanium dioxide, zirconium dioxide or beryllium oxide, or may be graphite or silicon carbide.

One suitable form of silica has an external surface area of approximately 1 $m.^2$ per g. Thus an effective catalyst consists of 5% palladium on silica, and this catalyst may be prepared by dissolving a palladium compound such as palladium chloride ($PdCl_2$) in the minimum amount of an acid, such as dilute hydrochloric acid; adsorbing this solution on finely powdered silica having an external surface area of approximately 1 $m.^2/g.$; evaporating to

dryness; and reducing the palladium chloride to palladium metal by means of hydrogen at a suitable temperature, for example, 50° to 400°C. More preferable catalysts are supported on silica-alumina, or silica-gel having a medium specific surface of 200 to 400 $m.^2/g.$

In the preferred method of carrying out the process, the supported catalyst is maintained in suspension in a liquid by vigorous agitation, and a mixture of hydrogen and oxygen preferably in equimolecular proportions is passed in. The hydrogen and oxygen may be diluted in order to decrease or remove the risk of accidental explosion; hence conveniently the oxygen is supplied as air. The process appears to be safe when using hydrogen-oxygen mixtures in the explosive range, provided the gas mixture does not come into contact with dry catalyst. The pressure and temperature at which the gases are passed into the solution may vary over a wide range.

Conveniently, the gases may be passed into solution at room temperature, but hydrogen peroxide is produced at a higher concentration if a lower temperature (for example, in the range 0° to −20°C. or below) is employed. If a higher total pressure than atmospheric (that is, 1 part hydrogen +4 parts air, giving a partial pressure of 0.16 atmosphere of each gas) is employed (for example, 75 atmospheres of a mixture of 4% hydrogen, 4% oxygen and 92% nitrogen, giving a partial pressure of 3 atmospheres for each gas), again hydrogen peroxide at a higher concentration is produced.

As a further feature, a process of oxidation is provided which comprises contacting an oxidizable substance in the liquid phase with hydrogen peroxide produced by contacting hydrogen and oxygen with a solid catalyst capable of promoting the combination of hydrogen and oxygen to hydrogen peroxide.

It is preferred that the hydrogen peroxide formed by the combination of hydrogen with oxygen should be contacted with the oxidizable substance very soon after it has been formed, for example in the reaction vessel in which it is being formed. Thus, in one form the oxidation process comprises passing hydrogen and oxygen into a water-containing liquid phase containing an oxidizable substance and a solid catalyst capable of catalyzing the combination of hydrogen with oxygen to give hydrogen peroxide.

It has been found advantageous in the oxidation process to promote the decomposition of the hydrogen peroxide in the presence of the oxidizable substance. Thus, the oxidation comprises contacting in a water-containing liquid phase hydrogen and oxygen with a solid catalyst capable of catalyzing the formation of hydrogen peroxide, contacting the formed hydrogen peroxide with an oxidizable substance, and promoting the decomposition of the hydrogen peroxide.

The decomposition of the hydrogen peroxide may be promoted by chemical means, for example by compounds which can enter into an electron transfer reaction with the hydrogen peroxide, or by radiation, for example ultraviolet light and high energy radiations such as X- and gamma-rays and the radiations such as alpha and beta particles produced in nuclear transformations.

The solid catalyst with which the hydrogen and oxygen are contacted to form hydrogen peroxide may itself act as the promoter of the decomposition of the hydrogen peroxide. It is,

however, preferred to have a separate promoter for the decomposition of the hydrogen peroxide: preferably in order to inhibit the decomposition of the hydrogen peroxide by the solid catalyst itself, there is present an acid or a second acid radical as previously defined, or a nonacidic oxygen-containing organic compound as previously defined, or more than one of these and the decomposition of the hydrogen peroxide is promoted by a homogeneous catalyst or by radiation.

It is believed that for the oxidation process the hydrogen peroxide molecules should decompose with the formation of at least one hydroxyl radical. When the electron transfer reaction mentioned above takes place, there is also formed a hydroxyl ion, according to the equation:

$$H_2O_2 + e^- \xrightarrow[\text{electron}]{} OH^- + OH^\circ$$

As examples of chemical compounds which can enter into an electron transfer reaction with hydrogen peroxide, may be mentioned salts of metals which are capable of existing in more than one valency state. Following the theory outlined above, such compounds promote the decomposition of hydrogen peroxide by providing a cation which by increasing its oxidation level provides the necessary electron. The overall electron transfer reaction is represented by the ionic equation:

$$H_2O_2 + M^{n+} \longrightarrow M^{(n+1)+} + OH^- + OH^\circ$$

In the above equation, M represents a transition metal. Conveniently the metal is in the lowest valency state in which it can exist as a cation. Of the transition metal salts, it is convenient to use the salts of the metals of Group VIII of the Periodic Table, particularly iron salts. Preferably the iron is in its divalent state. Other suitable metallic salts include salts of copper, silver, thallium, lead, antimony, bismuth, chromium and tin. The metallic salt is preferably a salt of an inorganic acid, provided that the anionic constituent of such a salt does not tend strongly to form an ionic complex with the cationic constituent of the salt. Sulfates are particularly convenient. A trace, for example 10^{-2} to 10^{-4} M of metallic salt is all that is normally required, but more than such a trace amount may be present if desired.

It is not always necessary for the liquid medium for this process of oxidation to contain an oxygen-containing organic compound, but when it is, ketones and alcohols are suitable. The concentration of such a compound is preferably as already described for the hydrogen peroxide formation process. Acetone is a particularly convenient ketone to use. When acetone is present in the liquid medium, it is necessary to ensure that the medium is not too acidic, for then the hydrogen peroxide decomposes by a side reaction and does not take part in the oxidation process. For example, when sulfuric acid is present in the liquid medium, the acid should preferably have a normality of less than 3, especially 0.01 to 2.

The conditions of temperature, pressure, nature and concentration of catalyst, of acid (if

any) and of second acid radical (if any) for the process of oxidation are the same as have been defined above for the hydrogen peroxide production process. The process of oxidation is applicable to inorganic and organic substances.

As examples of inorganic substances which may be oxidized, may be mentioned sulfonic acids, for example chlorosulfonic acid, from which results a mixture of the persulfuric acids, permonosulfuric acid H_2SO_5 (Caro's Acid) and per-disulfuric acid $H_2S_2O_8$. For these reactions no decomposition catalyst is necessary.

Organic substances which may be oxidized include aliphatic hydrocarbons, for example cyclohexane (to give cyclohexanol and cyclohexanone); aromatic hydrocarbons, for example benzene (to give phenol); and olefins, especially those containing up to 8 carbon atoms (to give the corresponding glycols, for example ethylene glycol, 1,2-dihydroxycyclohexane, asym-dimethyl ethylene glycol and trimethyl ethylene glycol). Advantageously hydroxylation catalysts, for example osmium tetroxide, vanadium pentoxide or molybdenum trioxide, may be present in the oxidation of olefins.

When the process is carried out in a liquid medium, the substance to be oxidized may be soluble in the liquid medium, but where it has only a limited solubility preferably it is emulsified. In one method of carrying out the above described oxidation process, the catalyst with which the hydrogen and oxygen are contacted to form hydrogen peroxide and the liquid medium containing the substance to be oxidized, are vigorously agitated together. The product of the oxidation process is separated from the liquid medium by, for example, distillation or liquid extraction, after sufficient reaction has taken place.

In another method of carrying out the oxidation process, the liquid medium containing the substance to be oxidized is passed over a bed of the catalyst countercurrent to a stream of hydrogen and oxygen.

As a particular feature, there is provided a process for producing an aromatic hydroxy compound, especially a phenol, which comprises contacting hydrogen and oxygen with a solid catalyst capable of catalyzing the formation of hydrogen peroxide; contacting the formed hydrogen peroxide with an aromatic hydrocarbon, and promoting the decomposition of the hydrogen peroxide. Preferably, the oxidation process is conducted in the liquid medium in which the hydrogen peroxide is produced, this medium preferably containing also an acid and a second acid radical as previously defined.

Thus, for example, there is provided a process for the oxidation of benzene to phenol which comprises passing a mixture of hydrogen and oxygen (as air) into a stirred mixture of benzene, aqueous sulfuric and hydrochloric acids, ferrous sulfate, and finely divided 5% palladium-on-silica catalyst. The product phenol is separated from the reaction mixture by solvent extraction. The process is illustrated by the following example.

A mixture of 1 part by volume of hydrogen and 4 parts of air at room temperature and atmospheric pressure was passed at a rate of 25 liters per hour into 50 ml. of an aqueous acetone solution (approximately 30 ml. of acetone) which was 10^{-2} N in hydrochloric acid and N in sulfuric acid, and in which was suspended 1 g. of finely divided 5% palladium-on-silica catalyst.

The gaseous mixture was passed into the solution for about 30 minutes, after which time 12.5 mg. of hydrogen peroxide was recovered.

The catalyst was prepared by dissolving palladium chloride ($PdCl_2$) in the minimum amount of dilute hydrochloric acid and applying the solution to finely powdered silica having an external surface area of approximately 1 $m.^2$ per gm. The solution was evaporated to dryness in a current of nitrogen at 60°C., and the palladium chloride reduced to palladium metal by heating in hydrogen at approximately 400°C.

In his earlier U.S. Patent 3,336,112 (44), G.W. Hooper described a rather similar H_2O_2 process, which was conducted with a solid catalyst having a metallic component selected from Groups I and VIII of the Periodic Table, in the presence of a stabilizing and activating salt of a condensed phosphoric acid having a polymerization number of up to 14.

PURIFICATION

DISTILLATION FOLLOWED BY TREATMENT WITH ACTIVATED CHARCOAL AT 0°C.

PPG (Columbia-Southern); Moore, J.W. (51): Where hydrogen peroxide is manufactured by oxidation-reduction of organic compounds, such as anthraquinone and hydrazobenzene, the resulting hydrogen peroxide solutions usually contain small amounts of carbon dissolved as an impurity. The nature of the carbon compounds which are present is not definitely known and, in many cases, the compounds are very difficult to identify. To some degree, the character of carbon compounds which are present depends upon the hydroquinone or other organic compound which is subjected to oxidation and also upon the organic solvent or solvents which are used in conjunction therewith. At all events, the product contains appreciable amounts of carbon in the form of dissolved carbonaceous compounds.

The removal of this carbon offers some difficulty. It is possible to distill a considerable amount of the hydrogen peroxide away from the carbon impurities. However, this results in the production of a more concentrated hydrogen peroxide. In most cases it is desired to avoid production of a concentrated impure hydrogen peroxide containing more than about 70% H_2O_2 in order to avoid the hazard of explosion which might take place as a consequence of reaction of the carbon compounds with hydrogen peroxide. Therefore, it has been necessary to purge at least a portion of the hydrogen peroxide from the distillation zone. This represents a substantial loss.

In this process, it has been found that carbon compounds, including compounds which are both more and less volatile than hydrogen peroxide, may be removed from hydrogen peroxide solutions of the type described above by contact with active carbon at a temperature below 10°C. and above the freezing point of the hydrogen peroxide solution, usually at about 0° C. By effecting contact of the hydrogen peroxide with the carbon at such temperature, the active carbon has been found to remove as much as 10% of its weight of carbon compounds from the hydrogen peroxide and thereby to produce a hydrogen peroxide solution of substantially improved purity.

It has been further found that little or no decomposition of hydrogen peroxide takes place during such contact. This is an extremely important factor since, when the active carbon is contacted with hydrogen peroxide at normal room temperatures, for example, 25° to 30° C., hydrogen peroxide decomposes to a very substantial degree. Such decomposition is naturally very disadvantageous from the economic point of view.

The process may be conducted in a simple manner by adding commercial grades of active carbon having absorbent properties to the hydrogen peroxide while the temperature is maintained below 10°C. and agitating the mixture for a period of time, usually in the neighborhood of 15 to 30 minutes or more. Coconut char is an especially effective type of charcoal used for this purpose. Other types of active carbon which are suitable include animal charcoal, wood charcoal, bone char, and the like.

In order to minimize decomposition of the hydrogen peroxide, it is found advantageous to treat hydrogen peroxide solutions containing less than about 40% by weight H_2O_2. An especially effective embodiment of this process involves treatment of purged streams resulting from the distillation of hydrogen peroxide. As has been stated above, it is rather common to distill hydrogen peroxide solutions by vaporizing an aqueous mixture of hydrogen peroxide, leaving a residue of a more concentrated hydrogen peroxide, usually containing in excess of 50 but rarely more than about 75% by weight of H_2O_2. Such solutions usually contain very large concentrations, for example, 5 to 50 grams per liter, of carbon.

The solutions may be treated with active carbon directly. In some cases, however, it has been found that an appreciable decomposition of hydrogen peroxide takes place in treating such concentrated solutions even when the treatment is effected at a temperature below 10°C. When this is observed, such residues may be diluted to concentrations below about 40%, usually in the range of 15 to 30% by weight H_2O_2, the impure hydrogen peroxide may be treated with active carbon at the temperature stated above, and a large portion of the dissolved carbon may be removed without appreciable decomposition of the hydrogen peroxide. The following example may further illustrate the procedure.

Hydrogen peroxide solution produced by the anthraquinone process contained 14.13% by weight of H_2O_2 and 1.60 grams per liter of total carbon. The solution was acidic, the acidity corresponding to 8.4 milliequivalents of acid per liter of solution.

The solution was cooled to 0°C. Subsequently, 50 grams of commercial active carbon, which is an absorbent prepared from "black liquor" obtained in pulping operations and sold under the trade name Nuchar C-190, was added to 2,000 grams of the cooled solution, and the mixture was stirred for 30 minutes while maintaining the temperature of the solution at 0°C. The mixture was then filtered while maintaining the mixture at 0°C., and the filtered hydrogen peroxide was analyzed for total carbon. The purified solution was found to contain only 0.29 gram per liter of total carbon and the acidic impurities had been almost completely removed. Quite obviously, at least a portion of the removed carbon compounds were acidic carbonaceous compounds.

When this process was repeated using another commercial activated carbon, known as Norit FQP, the resulting hydrogen peroxide solution was found to contain 14.11% H_2O_2 and the carbon content was only 0.07 gram per liter. The acidity of the solution was reduced to 0.8 milliequivalent of acid per liter of solution. In both of these cases, no substantial decomposition of hydrogen peroxide took place and substantial improvement in the color of the product, i.e., color removal, was achieved.

In some cases where the active carbon contains impurities which may tend to promote decomposition of hydrogen peroxide, the active carbon may be boiled in a strong acid, for

example, 10% nitric acid, for a substantial period of time, for example, two hours, and then the carbon may be recovered and washed with distilled water until the washings are neutral. Usually, however, this is not necessary.

The process may be performed readily at any convenient temperature below 10°C. In general, however, temperatures below about −25°C. are unnecessary since the removal has been observed to be less efficient at such temperatures than at higher temperatures.

EXTRACTION WITH OXYGEN-CONTAINING POLAR ORGANIC SOLVENTS

Shell Oil Co.; Hood, G.C., Smith, R.E., and Pierotti, G.J. (52): The purification of hydrogen peroxide initially present in aqueous mixture with reactive organic materials presents a number of distinctive problems, owing to the tendency of hydrogen peroxide to oxidize or otherwise react with such organic materials. Formation of difficultly separable complexes of hydrogen peroxide and oxygenated organic materials, or of organic peroxides, constitutes one of the problems. The danger of violent decomposition which is associated with the copresence of hydrogen peroxide and reactive organic materials presents another and a serious problem. There is also the likelihood of excessive losses of hydrogen peroxide (assuming that explosive decomposition can be avoided) caused by slow oxidation of the organic materials by hydrogen peroxide. On top of all this are the difficulties that are encountered when the organic impurities themselves are unstable, or labile; this difficulty is one of particular moment since the methods known in the art for recovery and purification of hydrogen peroxide are not well suited to its clean separation from labile organic materials which themselves undergo chemical change during the course of the separation.

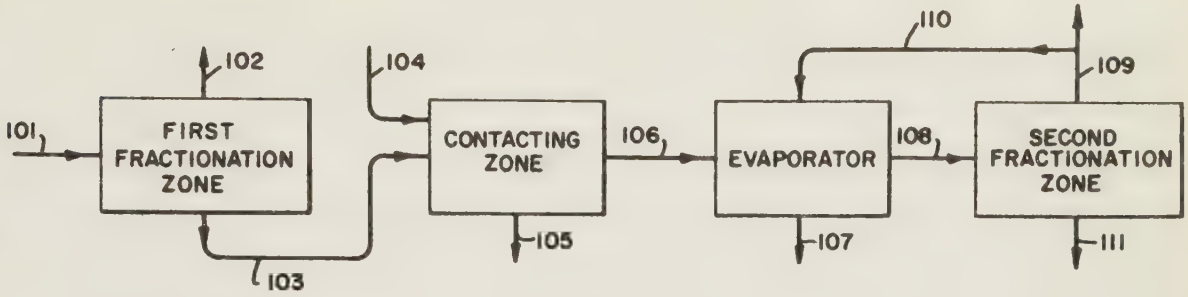
A process for purifying hydrogen peroxide, initially present in aqueous mixture with reactive organic materials, by employing such steps as fractionation, evaporation and steam-stripping requires careful design to avoid the hazards of violent decomposition mentioned above. It is customary to employ special safety measures wherever there is a chance, e.g., by malfunctioning of instruments or equipment, of building up a dangerous concentration of organic impurities in the presence of a high concentration of hydrogen peroxide. Such safety measures add substantially to the cost of a commercial installation.

In this process, the need for safety measures in purifying hydrogen peroxide containing organic impurities of peroxidic nature may be substantially reduced or avoided by selectively extracting the impurities from the aqueous hydrogen peroxide solution at an early stage in the process.

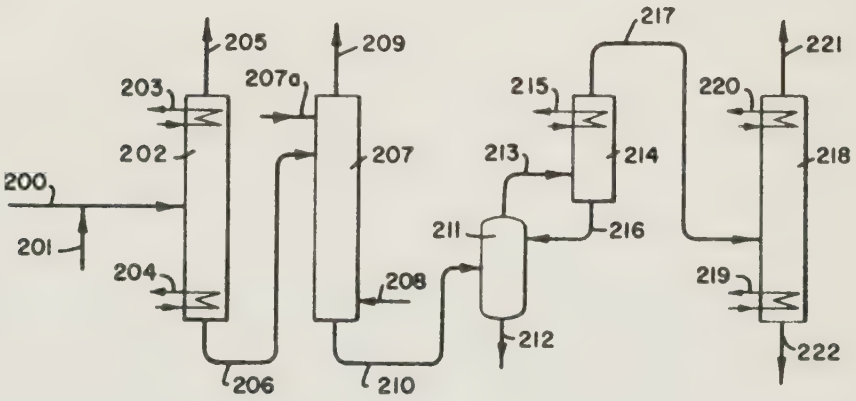
In its simplest modification, the process comprises contacting an aqueous solution of hydrogen peroxide containing the above mentioned organic impurities with a polar oxygen-containing organic solvent which is substantially immiscible with the solution, inert with respect to hydrogen peroxide and which has at least 4 carbon atoms per molecule, and then separating the substantially purified aqueous layer and the solvent layer containing the extracted impurities. The contact is preferably carried out in a multistage, countercurrent, liquid-liquid contacting zone, and the resulting raffinate and extract phases may be separately treated to recover solvent therefrom for reuse in the process. Purified aqueous hydrogen peroxide is recovered from the raffinate.

FIGURE 4.1: PURIFICATION OF HYDROGEN PEROXIDE BY EXTRACTION WITH OXYGEN-CONTAINING POLAR ORGANIC SOLVENTS

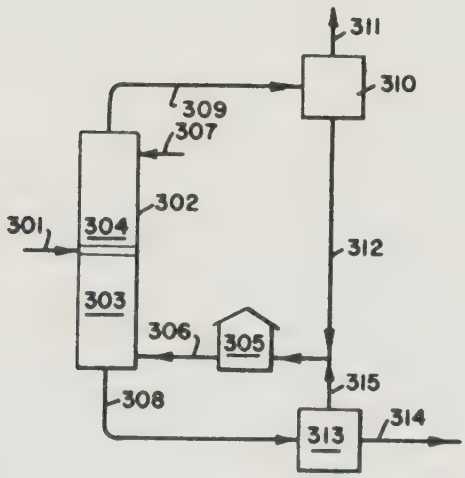
a.



b.



c.



Source: G.C. Hood, R.E. Smith, G.J. Pierotti, U.S. Patent 2,949,343, August 16, 1960

Referring to the drawings, Figure 4.1a shows a flowsheet of the purification process. Figure 4.1b shows equipment for carrying out the process. Figure 4.1c shows in greater detail equipment for carrying out the contacting and associated steps.

In Figure 4.1a, a schematic flow diagram of a suitable sequence of operations is shown. An aqueous mixture comprising hydrogen peroxide, lower aliphatic alcohol, particularly isopropyl alcohol, corresponding carbonyl compound, e.g., acetone when the alcohol is isopropyl alcohol, and other oxygenated organic compounds, is introduced into the purification system via line 101. Impurities which may be present include low molecular weight acids, alcohols, esters, aldehydes and ketones, organic peroxides and labile complexes of hydrogen peroxide with such oxygenated organic compounds. Inorganic compounds, such as salts, e.g., phosphates if a phosphate stabilizer has been included, may be present. The solution may contain from about 5% to about 20%, more typically from about 5% to about 12% hydrogen peroxide by weight, the balance being the organic materials in major amount and water in minor amount.

The solution is fractionated in the first fractionating zone to take overhead, via line 102, an aqueous mixture comprising the greater part of the alcohol and corresponding carbonyl compound. The fractionation is conducted under pressures between about 200 and about 1,000 mm. Hg and preferably under subatmospheric pressure between about 200 and about 700 mm. Hg in the presence of sufficient water (water being added if necessary) to allow the alcohol-water azeotrope to pass overhead and about 20 to 35% by weight aqueous solution of hydrogen peroxide to be withdrawn as bottoms product via line 103.

The liquid bottoms product from the first fractionation zone is conveyed via line 103 to the solvent contacting zone. A suitable solvent, which may be a monocarboxylic acid, monohydric alcohol, ketone or other suitable solvent as defined below, e.g., normal butanol, is introduced into the contacting zone via line 104. The solvent and aqueous solution of hydrogen peroxide are contacted, preferably in a countercurrent manner, and settled. The spent solvent, or extract, is removed via line 105 and the purified aqueous solution of hydrogen peroxide, or raffinate, via line 106. The solutions withdrawn via lines 105 and 106 may be separately treated in a suitable manner, e.g., by distillation or by extraction with benzene, to separate the solvent therefrom for reuse in the process.

The purified aqueous hydrogen peroxide solution is conducted via line 106 to an evaporator which is operated under a subatmospheric pressure preferably of about 100 to 250 mm. Hg. The solution is partially evaporated to leave a liquid residue containing between about 50 and about 65% hydrogen peroxide by weight which is withdrawn via line 107 and may be employed directly as a commercially useful product. The vapors, which have a composition determined by the vapor-liquid equilibrium for the hydrogen peroxide-water system at the pressure employed and the composition of the liquid residue, are conveyed via line 108 to the second fractionation zone, where they are rectified.

The overhead product withdrawn via line 109 comprises substantially only water, but may contain traces of volatile or organic materials which have not been removed in the previous steps of the process. A part of the aqueous overhead fraction may be condensed and recycled from the second fractionation zone to the evaporator via line 110. A purified concentrated aqueous solution of hydrogen peroxide, which may be of any desired concentration

in the range between 30 and 60% is withdrawn from the second fractionation zone via line 111. If it is desired to produce hydrogen peroxide of a higher concentration, say 90%, the product in line 111 may be passed to a second evaporation and fractionation stage.

It has been stated above that the crude hydrogen peroxide solutions contain, in addition to the alcohol and corresponding carbonyl compound, varying but appreciable amounts of other organic impurities including labile organic peroxides and complexes of hydrogen peroxide with oxygenated organic materials which are present. It has been ascertained that in the first fractionation zone there occurs, in addition to physical separation of alcohol and corresponding carbonyl compound from aqueous hydrogen peroxide, a partial degradation or decomposition of organic materials comprising peroxy oxygen, such as labile organic peroxides or complexes. Organic products of such degradation or decomposition are removed in part with the overhead fraction from the first fractionation zone and are conveyed in part with liquid bottoms product of the first fractionation step to the contacting zone.

In the contacting zone substantially all of the remaining organic impurities carried along in the aqueous hydrogen peroxide are extracted into the polar organic solvent which is substantially immiscible with the aqueous solution. If the solvent employed is of relatively low molecular weight within the suitable range, an appreciable portion may be dissolved in the aqueous phase. In that case, it may be desirable to treat the raffinate by a process such as distillation or solvent extraction to remove all solvent. If the solvent is relatively volatile and forms an azeotrope with water, e.g., n-butyl alcohol, the solvent may be permitted to remain with the aqueous hydrogen peroxide solution. In the evaporator a substantial portion of the hydrogen peroxide and water is ordinarily carried overhead into the second fractionation zone. Any relatively nonvolatile impurities present in the feed and not extracted in the contacting zone, e.g., inorganic impurities, will be carried out with the bottoms from the evaporator.

If a solvent such as n-butanol is present in the feed to the evaporator, it will be carried overhead into the second fractionation zone. Volatile organics which may have been carried through the process, and solvent such as n-butyl alcohol, are taken overhead with the water in the second fractionation zone, and a purified concentrated hydrogen peroxide solution may be withdrawn from the bottom or near the bottom of the second fractionation zone.

In the specific embodiment of the process illustrated in Figure 4.1b, the crude feed is introduced via line 200 into fractionating column 202, which is equipped with reflux inducing means 203, overhead line 205, reboiler or internally located coils 204 and bottoms product line 206. Reflux inducing means 203 may be an internal partial condenser or may represent an external reflux system comprising a condenser and suitable piping. In lieu of reboiler or heating coils 204, the lower end of column 202 may be heated by open steam. Inlet line 201 may be provided for introduction of diluent water. Column 202 may be a fractionating column of conventional design, such as a bubble-plate, grid-tray, packed or other suitable column constructed of materials such as porcelain, aluminum or stainless steel which are compatible with hydrogen peroxide solutions.

Column 202 is designed according to known methods for separation of the aqueous azeotrope of the alcohol overhead from water, with the additional feature that the tray capacity

together with the reboiler capacity are sufficient to give a residence time of the liquid below the feed plate between about 5 minutes and about 100 minutes, preferably between about 10 minutes and about 30 minutes. In column 202 the crude feed is fractionated at a maximum temperature (i.e., reboiler temperature) of at least about 85°C., preferably between about 90°C. and about 105°C. The pressure measured at the top of the column may be varied within limits according to the desired reboiler temperature and may be maintained within the range, for example, from about 400 to about 700 mm. Hg.

There is taken overhead from column 202 via line 205 a mixture of the secondary alcohol-water azeotrope and the ketone, together with a part of the organic impurities, e.g., esters, acids, and other carbonylic compounds. An aqueous solution of hydrogen peroxide is withdrawn as bottoms product from the column via line 206. The bottoms product preferably should contain between about 5% and about 35% by weight hydrogen peroxide, most desirably between about 20 and about 35% by weight. If the initial feed contains insufficient water for this, the readily calculable necessary amount of diluent water may be added via line 201.

Loosely bound complexes and other labile organic peroxide materials are largely but not wholly decomposed in column 202. Typical liquid bottoms product from column 202 will contain from about 2 to about 10% of organic materials based upon the weight of hydrogen peroxide in the product, which organic materials will include acids, esters, carbonylic compounds, alcohols, and peroxidic materials of varying degress of stability.

Liquid bottoms product from column 202 is conveyed via line 206 to contacting zone 207. This may contain conventional countercurrent, continuous, liquid-liquid extraction equipment such as a vertical column equipped with liquid distribution devices at the top and bottom to introduce feed and solvent, and internal liquid-liquid contacting devices such as bubble-plates, perforated-plates or other suitable devices; or zone 207 may represent a number of separate contacting and settling stages contained in separate vessels, in which the solvent and feed are conducted from one end to the other in opposing directions.

A suitable solvent, e.g., n-butyl alcohol, is introduced into contacting zone 207 through line 208. Organic impurities contained in the feed in line 206 are extracted therefrom by countercurrent contact with n-butyl alcohol. Purified aqueous hydrogen peroxide solution is withdrawn from zone 207 via line 210 while the extract, comprising solvent and organic impurities, is removed via line 209. The extract may be washed in a washing stage of contacting zone 207 with a suitable wash liquid, e.g., pure water, which may be introduced via line 207a, to remove residual hydrogen peroxide from the extract.

The extract withdrawn by line 209 may be treated in equipment not shown, e.g., by distillation or solvent extraction, to recover solvent for reuse in the process and a concentrate of organic impurities which may be discarded. Any peroxide present in the discard stream may be destroyed, if desired, e.g., by treatment with sodium hydroxide. The purified aqueous hydrogen peroxide solution in line 210 may contain some dissolved solvent. It may be treated in equipment not shown, such as by distillation or solvent extraction, to remove solvent for reuse in the process, or it may be directly charged to evaporator 211. Evaporator 211 may be equipped with lines and pumps, not shown, to continuously circulate liquid out of and back to it in order to insure the desired low residence time in the evaporator.

Evaporator 211 may be an evaporator of known design, such as a tubular evaporator, constructed preferably of stainless steel so as to minimize decomposition of the hydrogen peroxide during evaporation. Evaporator 211 is operated at a reduced pressure, preferably between about 100 and about 250 mm. Hg, and the feed rates to the evaporator system and the rate of withdrawal of the liquid residue (via line 212) may be adjusted to yield a liquid evaporation residue containing between about 50 and about 65% by weight hydrogen peroxide, or, more broadly, between about 40 and 65% by weight.

The vapors evolved in evaporator 211 are passed through line 213 to a short fractionating column 214 which may be termed a knock-back column, where they are partially condensed by the cooling action of water circulated through internal condenser 215 or by water directly injected into the top of the column, and the condensate returned to evaporator 211 via line 216. The vapors entering column 214 via line 213 comprise a vaporous mixture of water and hydrogen peroxide and may further contain small amounts of volatilized organic impurities which were not extracted in zone 207 and vaporized solvent such as n-butyl alcohol which was not removed from the raffinate obtained in zone 207. By partially condensing these vapors, with rectification, traces of organic impurities will be returned to the condensate and thereby substantially excluded from the vapors of hydrogen peroxide and water which are conveyed to the subsequent concentration column 218.

Furthermore, by insertion of a partial rectification column 214 between evaporator 211 and column 218, possible entrainment of impurities in the vapors entering column 218 is minimized. If the contacting system operating in zone 207 is adequately designed and a suitable solvent employed, substantially no volatile organic impurities will be retained in the raffinate stream and column 214 may then be replaced by a simple knockout drum or equivalent entrainment removing means, operating without rectification. When knock-back column 214 is employed, including rectification, it may be a grid-tray, bubble-plate, packed or equivalent column. It should have a capacity of from about 2 to about 7 theoretical plates in order to obtain the desired concentration of and rejection of organic impurities into the liquid residue from the evaporation step, and should be operated at a reflux ratio (reflux/feed, weight basis) of from about 0.05 to about 0.20.

Vapors leaving the top of column 214 are conveyed through line 217 into fractionating column 218, provided with internal reflux condenser 220, overhead line 221, reboiler or heating coils 219, and bottoms line 222. Column 218 may be a fractionating column designed from known principles for rectification and concentration of vaporous mixtures of water and hydrogen peroxide, water being taken overhead and concentrated hydrogen peroxide solution being withdrawn as bottoms product. Column 218 is operated at pressures generally corresponding to those in the evaporator system, taking into account slight pressure drops through the connecting conduits, etc. For example, with vacuum being applied by vacuum pumps (not shown) or barometric condensers (not shown) on line 221, column 218 may be operated at a pressure, measured at the top, of 100 mm. Hg, and a pressure, measured at the bottom, of 130 mm. Hg; column 214 may be operated at a mean pressure of 160 mm. Hg; and evaporator 211 may be operated at a pressure of about 170 mm. Hg.

When solvent such as n-butyl alcohol is present in the charge to column 218, all of the alcohol will be taken overhead admixed with water, via line 221, as azeotrope of the alcohol. The hydrogen peroxide solution withdrawn from column 218 via line 222 may

contain from about 30 to about 60% by weight hydrogen peroxide. This is a pure solution of hydrogen peroxide which may be employed for commercial purposes or, if desired, may be charged to second evaporation and fractionation stage, not shown, for further removal of water and recovery of more highly concentrated aqueous hydrogen peroxide, e.g., up to 90% or higher, as bottoms product.

A preferred method of operating the solvent contacting zone 207 in Figure 4.1b is illustrated by means of the schematic flow diagram in Figure 4.1c. An aqueous hydrogen peroxide solution comprising organic impurities, such as the bottoms product from column 202, is introduced via line 301 into solvent extraction zone 302. This may be a continuous countercurrent liquid-liquid extraction apparatus, such as a tower equipped with suitable liquid distribution and redistribution devices, known to the art. The tower may comprise an extraction zone 303 and an extract washing zone 304. Solvent is introduced into zone 303 from solvent storage tank 305 via line 306. The solvent may suitably be n-butyl alcohol. Countersolvent, which may suitably be water, may be introduced into zone 304 via line 307.

In zone 303 the aqueous hydrogen peroxide solution moves downward countercurrently to the solvent. Purified aqueous hydrogen peroxide solution is taken out through line 308. Due to gravity differentials, the solvent extract continues to move up the column through zone 304. Countersolvent, such as water, introduced through line 307, washes out of the extract any hydrogen peroxide which may be dissolved. The hydrogen peroxide-free extract leaves the column via line 309 and may be passed to solvent separation zone 310 which may suitably be a distillation zone, or a solvent extraction zone in which a suitable second solvent, such as benzene is employed to dissolve the first solvent selectively, followed by a distillation to separate benzene and solvent. In any case, the separated impurities are ultimately withdrawn from the system via line 311 and the recovered solvent is returned to solvent storage tank 305 via line 312.

The raffinate removed from column 302 via line 308 may be passed to raffinate treating zone 313 where it may be subjected to azeotropic distillation in which an azeotrope of n-butyl alcohol and water is taken overhead and aqueous hydrogen peroxide is withdrawn to be passed to an evaporator, such as 211, via line 314. Instead of a distillation zone, 313 may represent a solvent extraction zone in which a suitable second solvent such as benzene is employed to extract n-butyl alcohol from the aqueous hydrogen peroxide. In either case, the resulting solution of n-butyl alcohol, after separation from the aqueous hydrogen peroxide, is further treated, as by distillation, to recover n-butyl alcohol for return to solvent tank 305 via line 315.

The typical feed from which hydrogen peroxide is recovered and purified according to the process as described by means of Figure 4.1c will be a product that has been prepared by partial oxidation of a lower secondary aliphatic alcohol under conditions which direct the oxidation to yield hydrogen peroxide rather than water as the normal coproduct of the oxidation, the organic oxidation product being the ketone which corresponds to the secondary alcohol. The crude feed preferably will contain isopropyl alcohol as the lower aliphatic secondary alcohol and acetone as the corresponding carbonyl compound. Instead of isopropyl alcohol and acetone, secondary butyl alcohol and methyl ethyl ketone may be present as the alcohol and carbonyl compounds respectively.

A typical feed will contain from about 1% to about 20% by weight hydrogen peroxide, from about 40 to about 90% by weight isopropyl alcohol, an amount of acetone approximately stoichiometrically equivalent to the hydrogen peroxide, a minor amount of water compared to the isopropyl alcohol and other organics, and the feed will include organic peroxides varying in amount from about 1% by weight of the hydrogen peroxide to an amount about equal to the hydrogen peroxide. A feed such as described is not charged directly to the solvent extraction of the process but is first subjected to fractionation, such as in column 202. Substantially all the alcohol and the corresponding ketone are removed overhead in such distillation and a substantial portion of organic peroxides may be decomposed during that distillation process.

The aqueous hydrogen peroxide solution removed as bottoms product from the first distillation contains organic impurities whose exact chemical structures have not been determined. These impurities are of relatively low volatility with respect to hydrogen peroxide. Chemically they appear to behave like a hydroxyhydroperoxide molecule. Such a molecule may be formed by the reaction of a carbonyl compound with hydrogen peroxide. Upon thermal treatment of the impurities, formaldehyde, formic acid, acetaldehyde and acetic acid may be found as degradation products.

The solvents suitable for use in the process are polar organic solvents capable of hydrogen bonding, substantially immiscible with aqueous hydrogen peroxide solution, and substantially chemically inert to hydrogen peroxide, i.e., nonreactive therewith. Suitable solvents are organic compounds containing only carbon, hydrogen and oxygen, having the oxygen directly bonded to only a single carbon atom, and having at least 4 carbon atoms per molecule. Monofunctional compounds such as monohydric alcohols and monocarboxylic acids are ordinarily preferred, because the polyfunctional compounds tend to be too water-soluble. As the number of carbon atoms per oxygen atom in the solvent increases, the solubility of the impurities in the solvent decreases so that more solvent is required for effective extraction. Hence, it is not desirable to employ as oxygenated monofunctional solvents compounds having more than about 12 carbon atoms per molecule. Especially preferred solvents are normal butyl alcohol, isoamyl alcohol and caproic acid.

Essentially nonpolar solvents, such as hydrocarbons, including aromatics, ethers, and chloroform, have been found entirely ineffective for the extraction of carbonaceous impurities from aqueous hydrogen peroxide as described. Aldehydes, though polar in nature, proved too reactive with hydrogen peroxide to be satisfactory. They are readily subject to conversion to acids.

Among the suitable solvents are alcohols such as n-butyl alcohol, isoamyl alcohol, cyclohexanol, methyl cyclohexanols, n-heptyl alcohol, n-octyl alcohol, 5-methyl hexanol, 2-heptanol, 3-methyl-3-heptanol and the like; carboxylic acids such as butyric acid, valeric acid, caproic acid, heptanoic acid and the like; ketones such as methyl propyl ketone, methyl isobutyl ketone, diisopropyl ketone, diisobutyl ketone and the like; and esters such as isoamyl acetate, butyl acetate and propylpropionate.

The conditions suitable for the various distillation and evaporation steps which may be associated with the solvent extraction process have been presented above in the description of the process of Figure 4.1b. The solvent extraction step itself may be carried out at

substantially atmospheric temperature and pressure or at temperatures varying in the range between slightly above 0°C. and 120°C. The bottoms from tower 202 may, for instance, be contacted with solvent substantially at the temperature at which they leave the column, which may be in the range between 85° and 120°C. A preferred temperature range for the solvent extraction is between 10° and 60°C. The pressure may be any pressure at which the feed and solvent remain in liquid phase, but it will preferably be in a range between the pressure prevailing at the bottom of column 202 and about 760 mm. Hg.

The number of stages of contact to be employed and the ratio of solvent to feed to be employed will be determined according to well-known principles of solvent extraction. From 10 to 30 stages of countercurrent contact will generally be found sufficient for extraction of substantially all of the organic impurities from the aqueous hydrogen peroxide. The solvent to feed ratio will be in the range between 0.5:1 and 10:1.

In general, it will be found that an appreciable amount of hydrogen peroxide will dissolve in the solvent during the contacting step. It will therefore be desirable to use a countersolvent or wash solvent to remove such hydrogen peroxide from the solvent and return it to the raffinate. Water is ordinarily employed as the wash solvent. In the process of Figure 4.1b, a portion of the water leaving product fractionator 218 through line 221 may be condensed and employed as the countersolvent in the solvent extraction zone, i.e., that which is added through line 207a. The ratio of countersolvent to solvent will desirably be relatively small, in the range from 0.1:1 to 0.5:1.

The solvent extraction process will be commercially attractive only if the solvent can be recovered from the extract stream, and also from the raffinate stream if it is present in appreciable concentration. Methods of recovering the solvent may vary with its chemical identity and will readily occur to the skilled chemist or chemical engineer. For example, when the solvent is n-butyl alcohol a suitable method of separating it from the peroxidic and acidic impurities which it has extracted is by distillation in a separate fractionation zone in which caustic, such as sodium hydroxide, is maintained in the still pot or reboiler to neutralize the acids and prevent their decomposition. The n-butyl alcohol may be recovered as overhead product, and the impurities as bottoms product.

Another suitable method may be to first contact the extract stream with aqueous caustic to neutralize and partially extract the acids and then extract the nonaqueous layer with a suitable second solvent, e.g., benzene, which dissolves the normal butyl alcohol. The liquid layers are then separated and the benzene layer is subjected to distillation to recover normal butyl alcohol and benzene suitable for reuse in the processes.

Since normal butyl alcohol is approximately 7% soluble in water, it will also be desirable to recover it from the raffinate. This may be done by a simple countercurrent liquid-liquid extraction with benzene which will readily extract the normal butyl alcohol. The alcohol and benzene are separated by distillation. Another suitable method of recovering normal butyl alcohol from the raffinate is by steam-stripping.

Extraction experiments were carried out by contacting various volumes of aqueous hydrogen peroxide, containing peroxidic organic impurities and produced by a process of controlled oxidation of isopropyl alcohol, with various volumes of several different solvents under

vigorous agitation for 10 to 15 minutes. After the layers had separated, samples of each were withdrawn and analyzed for hydrogen peroxide, total carbon and acids. The runs were carried out at room temperature. The results are presented in Table 4.1, in which the first column shows the class of solvent, the second column the identity of the solvent, the third column the solvent-to-feed ratio employed, the fourth and fifth columns the equilibrium constant "K" for organic impurities and hydrogen peroxide respectively, and the sixth column the "beta" value, which is the ratio of the equilibrium constants expressed as $K_{impurities}/K_{H_2O_2}$. The equilibrium constant is defined by the equation:

$$K = \frac{\text{Concentration of component 1 in phase 1}}{\text{Concentration of component 1 in phase 2}}$$

TABLE 4.1: EQUILIBRIUM CONSTANTS AND BETA VALUES

Class of Solvent	Solvent	Solvent: Feed Ratio	$K_{impurities}$	$K_{H_2O_2}$	Beta Value
Acid	Caproic Acid	5	0.30	0.03	10
Alcohol	Isoamyl alcohol	1	0.43	0.23	1.9
Do	n-butyl alcohol	1	0.85	0.42	2.0
Do	n-heptyl alcohol	1	0.35	0.15	2.3
Do	p-methyl cyclohexanol	1	0.53	0.25	2.1
Ketone	methyl isobutyl ketone	5	0.27	0.16	1.7
Do	diisobutyl ketone	5	0.05	0.03	1.7
Ester	isoamyl acetate	1	0.16	0.11	1.5
	diethyl phthalate	5	0.09	0.05	1.8
Nonsolvents:					
Hydrocarbon	Benzene	1	0	0	--------
	Hexane	1	0	0	--------
Ether	Diisopropyl ether	5	0.04	0.06	0.6
Chloroform	Chloroform	1	0	0	--------

The data show that organic impurities are preferentially extracted from aqueous hydrogen peroxide solutions by the polar solvents such as acids, alcohols, esters and ketones; this is indicated by the fact that the beta value is greater than 1 for each of these materials. There is no substantial difference with respect to selectivity between the various solvents, except that caproic acid appears to be substantially more selective than the others.

The capacity of the various solvents for organic impurities is indicated by the "K" value in the fourth column. It is seen that the alcohols have the relatively greatest capacity. Therefore less volume of solvent will be required when employing alcohols. Normal butyl alcohol is particularly outstanding, with a "K" value almost twice that of any other solvent tested. Hydrocarbons, specifically benzene and hexane, extracted no organic impurities; neither did chloroform. Diisopropyl ether had a beta value less than one, and thus tends to be a selective solvent for hydrogen peroxide, rather than for the organic impurities.

From the data in Table 4.1, suitable conditions for solvent extractions systems employing the various solvents are readily calculated. For example, the approximate conditions for a solvent extraction system such as illustrated in Figure 4.1c, using isoamyl alcohol as the solvent introduced by line 306 and water as the counter solvent introduced by line 307, are given in Table 4.2.

TABLE 4.2: CONDITIONS FOR SOLVENT EXTRACTION SYSTEM

t, °C.	Feed			Theoretical Stages		Solvent/Feed		Recovery, Percent H_2O_2	Purity * Percent wt. H_2O_2
	Percent wt. H_2O_2	Percent wt. C	Percent wt. H_2O	Absorber	Stripper	Water	Alcohol		
25	30.00	1.00	69.00	10	10	1.4	5	99.0	99.6

* With respect to organic impurities (corresponds to an 88 percent rejection of the organic impurities).

The results show that with a relatively large number of extraction stages the desired separation can be successfully accomplished with a reasonable solvent to feed ratio. If a greater amount of solvent is employed, less extraction stages will be required.

COMBINED FREEZING, CRYSTALLIZING AND WASHING TECHNIQUE

Laporte Chemicals Ltd.; Holmes, W.R., Marshall, J.G., and Oates, A.E. (53): This process is only applicable to hydrogen peroxide-water mixtures containing at least 61.2% of hydrogen peroxide weight for weight. Processes of the kinds described above do not produce mixtures containing such high concentrations of hydrogen peroxide, and the standard method of achieving such concentrations is by distillation. During fractionation under vacuum of aqueous hydrogen peroxide solutions made by the hydrolysis of inorganic per-compounds most of the impurities remain in the boiler residue, but small fractions pass over either into the overhead waste product or into the fractionated product by virtue of either entrainment of liquid or the volatility of the impurities.

In the case of hydrogen peroxide made by an organic process, however, the volatility of the organic impurities may be such that a far greater proportion finds its way either into the overhead waste product or into the fractionated product though, of course, the points at which these impurities appear depend upon their several volatilities. Thus, where aqueous hydrogen peroxide from the aqueous extraction column of a cyclic process is fractionated, the dissolved solvents, if normally steam-volatile are largely recovered in the overhead product, but the degradation compounds appear in the fractionated product or remain in the boiler residue.

Thus, both the fractionated product and the boiler residue may contain either inorganic or organic impurities or both and, provided the hydrogen peroxide content of the aqueous solution is above 61.2% of hydrogen peroxide weight for weight, it has been found that purification is possible by means of a combined freezing and washing technique.

Several methods have previously been proposed for reducing the impurities, particularly inorganic impurities, in aqueous solutions. Treatment with an adsorbent solid such as active carbon in the form of finely divided charcoal has been suggested and so has solvent extraction. There are, however, inherent disadvantages in both these processes; and especially with solvent extraction, when treating aqueous solutions of hydrogen peroxide containing more than 60% hydrogen peroxides weight for weight, since the risk of fire is considerable.

Purification

It has now been found that by washing crystals, formed on cooling aqueous solutions of hydrogen peroxide containing impurities, with aqueous solutions of hydrogen peroxide of substantially the same concentration as the mother-liquor, but containing substantially less or none of the impurities, a high degree of purification is obtained.

Preferably the formation and washing of the crystals are carried out in an isothermal column, the passage of liquor in the column being countercurrent to the passage of crystals.

Referring to Figure 4.2a, this drawing, with the exception of the line of alternate dots and dashes to which reference is made below, is taken from Hydrogen Peroxide, by W.C. Schumb, C.N. Satterfield and R.L. Wentworth (74). The results of various investigators showed that hydrogen peroxide had the freezing characteristics shown by the solid curves in the graph. Thus, if, for example, a solution of concentration X is cooled to temperature $-Y°$, a solid consisting of pure hydrogen peroxide will separate out leaving a mother-liquor of composition B. The solid phase, being denser than the liquid phase, will fall down through the liquid phase and settle as a bed at the bottom of the vessel.

In carrying out the process, the aqueous hydrogen peroxide washing solution is derived from a source exterior to the vessel in which the crystallization is being effected. The washing solution is usually fed into the column employed for carrying out the process at the same temperature as that of the mother-liquor into which it is fed in order to ensure that the washing solution is in equilibrium with the crystals at the point of entry. The mass of crystals of 100% hydrogen peroxide formed upon cooling has associated with it a certain proportion of the mother-liquor which is removable by conventional methods only with very considerable difficulty.

Since the crystals are 100% hydrogen peroxide and contain no impurities, the washing of the crystals with an aqueous solution of hydrogen peroxide reduces the concentration of the impurities in the associated mother-liquor, giving a purified product. Therefore, the substantially vertical line of alternate dots and dashes in Figure 4.2a is representative of the fact that crystals of 100% hydrogen peroxide are formed. Purification by freezing and washing will, of course, be achieved if the above theory is incorrect, and the utility of the process is in no way affected by the correctness or otherwise of the theory. It should be noted that the process is not applicable to cases where the impurities themselves crystallize out or are deposited in the cooling of the hydrogen peroxide-water mixtures. Colloidal separation of the impurities is, however, permissible since colloidal particles will be removed by the wash solution.

The actual temperature to which the aqueous solution of hydrogen peroxide to be purified has to be cooled in order to secure the production of crystals is easily obtained by reference to Figure 4.2a. Thus, in the example given previously, a solution of concentration X has to be cooled to temperature $-Z°$ to secure any formation of crystals, but in order to secure substantial formation it is cooled to a temperature below this and the temperature given in the foregoing example was $-Y°$.

Referring now to Figure 4.2b, the solution to be purified, e.g., 85% aqueous hydrogen peroxide, is fed into the apparatus at A, the temperature maintained in the zones C_1C_2 and C_2C_3 being about $-30°C$. (the cooling being provided by refrigerant passing through coil R

FIGURE 4.2a: FREEZING CURVES FOR H_2O_2 - H_2O SOLUTIONS

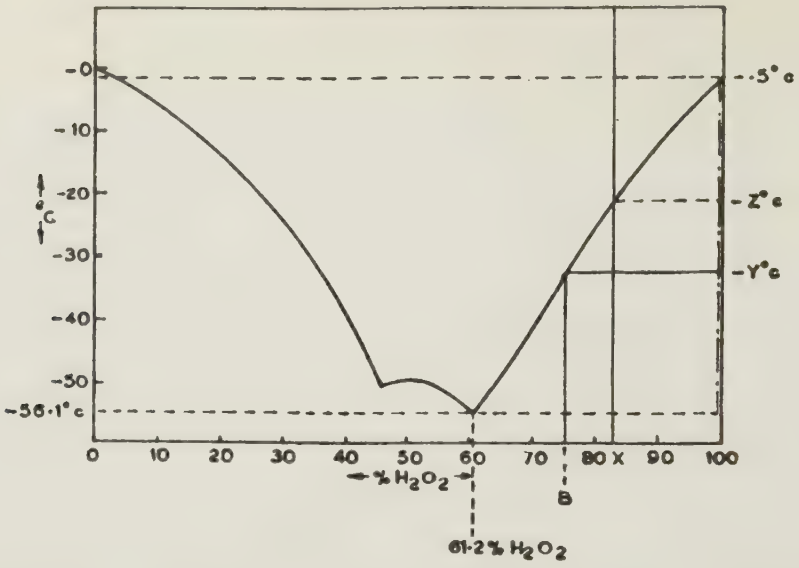
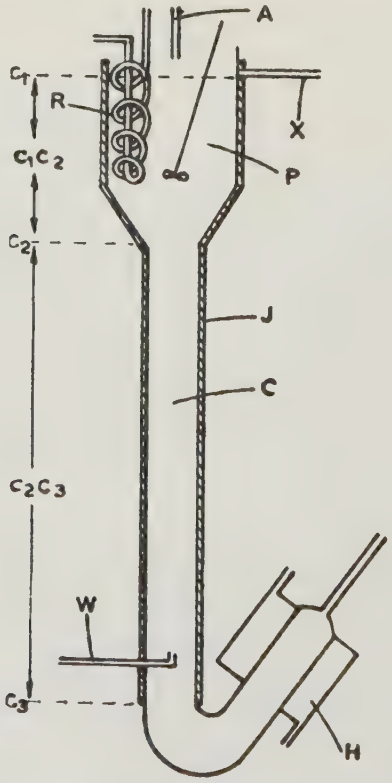


FIGURE 4.2b: VERTICAL SECTION THROUGH APPARATUS SUITABLE FOR PURIFICATION BY COUNTERCURRENT WASHING



Source: W.R. Holmes, J.G. Marshall, A.E. Oates, U.S. Patent 3,010,808, November 28, 1961

and insulation being provided by jacket J). The crystals form in zone C_1C_2 in which is disposed a continuously rotating agitator P, and fall and settle into zone C_2C_3. The level of the contents is kept constant by the mother-liquor (about 76% hydrogen peroxide in this case) overflowing through X, a filter (not shown) being fitted to prevent crystals leaving the apparatus through X.

A bed of crystals forms in zone C_2C_3 extending round the bend at the base of column C, and the pressure of the falling crystals drives this bed into a heat exchanger H which is maintained at a temperature high enough to melt all the crystals (e.g., by water at +15°C.). The bend in the tube has been found necessary in practice to prevent the solution formed in heat exchanger H from passing up through the bed of crystals and being lost in the mother-liquor. Since it is an isothermal column no variation in hydrogen peroxide concentration in the liquor or crystals occurs at any stage, and there is no temperature gradient other than the sharp rise as the bed of crystals enters the heat exchanger H.

The washing solution is introduced through the tube W at −30°C. and is of the same concentration as the mother-liquor (in this case approximately 76% hydrogen peroxide weight for weight). It reduces the concentration of impurities in the liquor; thus, the crystals leaving the bottom of zone C_2C_3 for the heat exchanger H take with them a hydrogen peroxide solution of reduced concentration of impurities.

The passing of liquor being in an upwards direction by virtue of the overflow through X, it will be appreciated that such a column may be operated in two ways, but the general principle of crystals passing through a mother-liquor of progressively decreasing impurity concentration applies. Not only can washing solution be made to percolate upwards through a packed column of crystals, but also the crystals can be made to fall freely through the liquor until they collect at the bottom of zone C_2C_3 and below the point of entry of the tube W. This overflow thus consists of washing solution and the liquor produced by the crystallization of the fresh 85% hydrogen peroxide feed material.

It should be noted that the final concentration of the hydrogen peroxide obtained after melting of the crystals in heat exchanger H is dependent upon the amount of liquor taken out with the crystals. The degree of purification obtained depends on (1) the ratio of the amount of washing solution to the amount of mother-liquor reaching the heat exchanger with the crystals, (2) the column length, (3) the liquid flow rates, and (4) the operating temperature. The amount of liquor extracted with the crystals upon melting is capable of determination (see below), the washing ratio, defined as:

$$\frac{\text{Volume of washing solution}}{\text{Volume of liquor extracted with crystals}}$$

is also capable of determination. Plainly, the greater the washing ratio the greater the purification, though obviously for a practical system there are limits to the amount of washing solution that may be employed. The washing ratio being controllable, the degree of purification obtained is also controllable.

The amount of liquor present in the crystals (the runoff) as they leave the column is calculated as follows. The hydrogen peroxide concentration is determined by the standard method of

titrating with potassium permanganate. The runoff (before melting) is assumed to consist of solid 100% hydrogen peroxide plus liquor, the concentration of this liquor being determined by the temperature at which the process is operated. Knowing the concentration of each of the two components and the concentration of the final mixture, the proportion of the two components can be calculated.

A portion of the product may be used as the basis for the washing solution. The portion of the product to be used in this manner is diluted with distilled water to the concentration of the mother-liquor cooled to operating temperature and fed to the column C through the tube W. The maximum washing ratios which can be obtained in this way are those corresponding to the return of all the product to the column in the form of washing solution; of course, in a practical system, the return of all the product is not envisaged. Assuming that the fraction of liquid in the product leaving the bottom of the column is 40% by weight, calculated as shown before (the liquor fraction will not always be 40%), the maximum washing ratios are as listed in Table 4.3.

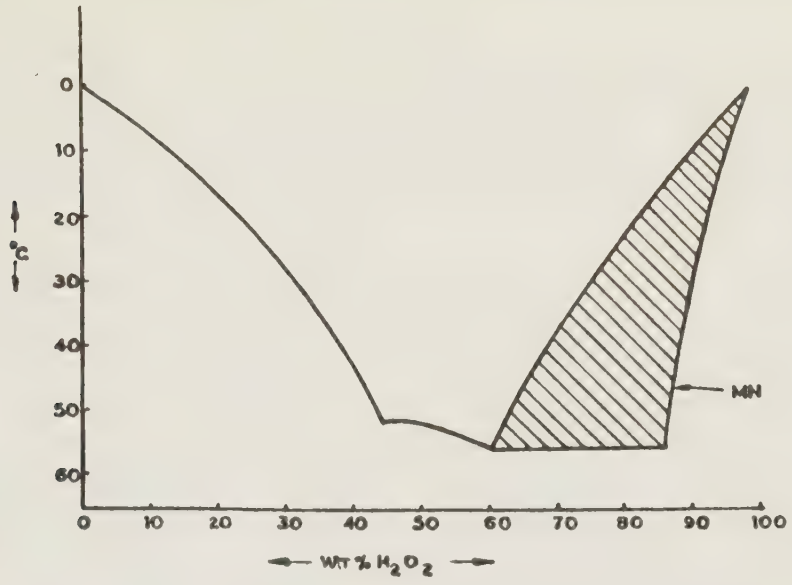
TABLE 4.3: MAXIMUM WASHING RATIOS

Temperature, ° C.	Corresponding liquor concn., H_2O_2 percent	Product H_2O_2 concn., percent	Maximum washing ratios
−5	95.6	98.2	2.57
−10	91.3	96.5	2.64
−15	87.3	94.9	2.72
−20	83.4	93.3	2.80
−25	79.8	91.9	2.88
−30	76.5	90.6	2.96
−35	73.3	89.3	3.05
−40	70.2	88.1	3.14
−45	67.2	86.9	3.23
−50	64.5	85.8	3.32
−55	61.7	84.7	3.43
−56.1	61.2	84.5	3.45

Thus, in order to obtain purified product from the system, the washing ratios should not equal or exceed the figures given above for the temperatures and concentrations to which they relate. For washing ratios below 1, a maximum purification exists for any given washing ratio and, provided the column length is sufficient for the purification to reach this maximum, the degree of purification depends only on the washing ratio. For washing ratios above 1, there is no maximum, the purification increasing with both washing ratio and column length.

In actual operation of the countercurrent column, a certain proportion of the liquor must be run off from the base of the column in order to obtain in the product all the material crystallized in the crystallizer. The proportion of liquor required increases with the throughput of the column, but in no case does it fall below 38% by weight. When hydrogen peroxide is crystallized, a proportion of solid 100% hydrogen peroxide is formed; and this fraction increases as the temperature of crystallization decreases below the freezing point. There is thus a minimum practical temperature of crystallization for any given hydrogen peroxide concentration of feed. Conditions represented by the area to the right of the line MN, shown in Figure 4.2c, which is the freezing point/composition graph for hydrogen peroxide-water mixtures, give less than the above required proportion of liquid, and thus the practical

FIGURE 4.2c: FREEZING POINT COMPOSITION RELATIONSHIP FOR THE H_2O_2-H_2O SYSTEM INDICATING THE WORKING AREA FOR A PRACTICAL SYSTEM



Source: W.R. Holmes, J.G. Marshall, A.E. Oates, U.S. Patent 3,010,808, November 28, 1961

conditions of operating for the countercurrent method are represented by the shaded area. The process is not limited to operation in a countercurrent washing device. An alternative method of operating is to use a continuous rotary filter consisting of a drum slowly rotating, the surface of the drum being formed by a filter medium stretched over a supporting structure. A portion of the drum surface is in contact with a crystal slurry of hydrogen peroxide crystals in a mother-liquor of aqueous hydrogen peroxide, the actual portion altering as the drum rotates. The slurry can be in contact with either the top or bottom of the drum.

The interior of the drum is divided radially into sections, and suction and air pressure can be applied to each section in turn. Thus the section in the slurry and several that have just passed through it have suction applied, so that crystals adhere to the drum surface and the liquor is filtered off. In a later section, washing solution is fed onto the adhering crystals and suction applied inside. A later section has compressed air applied to cause the crystal cake to leave the drum and be collected.

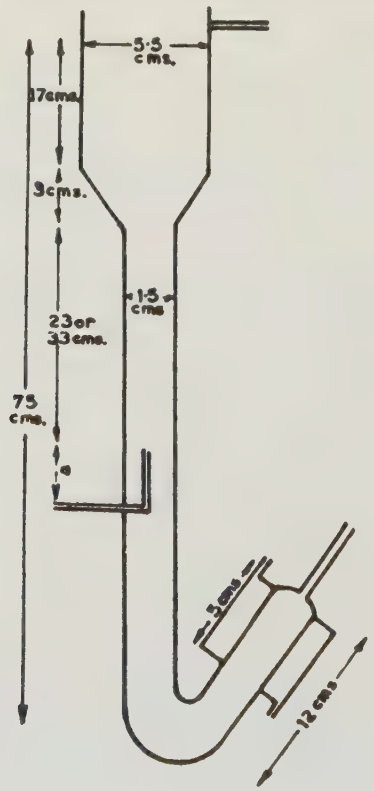
This method of operation has the advantage that smaller amounts of washing solution are needed than in countercurrent washing, since a far greater proportion of mother-liquor is removed during filtration than occurs in the settling of the countercurrent washing method. A higher degree of purification is therefore achieved for a given return of product hydrogen peroxide as washing solution. A disadvantage of this system is that, in addition to having to handle solids, the whole of the process must be carried out at a temperature below the freezing point of the hydrogen peroxide feed.

Centrifuging of the crystal slurry prior to washing of the crystals is another method of operation. In this case, even more mother-liquor is removed from the crystals prior to the application of the washing solution, thus further decreasing the amount of washing solution required.

Where the filtration or centrifuging methods are used, the crystal slurry has to be fed from a crystallizer to the filter or centrifuge and a limit is set by the minimum fraction of liquor needed for recovery of all the crystals formed in the crystallizer. Thus, again, as in the countercurrent washing method, the shaded area in Figure 4.2c is representative of the conditions for practical working.

It will be appreciated that the overflow of mixed mother-liquor and washing solution from the countercurrent washing system and the filtrates of mother-liquor and washing solution from the methods based on filtration and centrifuging must not be discarded in any practical process. Those liquors are therefore concentrated to the original feed concentration and fed to the crystallizer, a purge being provided as an outlet for impurities. This concentration may be in accordance with U.K. Patent 590,439, which embodies a system for purging a substantial proportion of the impurities in the feed, but for reasons stated does not eliminate all the impurities. The following example illustrates the process. The experimental results given were obtained using the apparatus illustrated in Figure 4.2d.

FIGURE 4.2d: APPARATUS USED TO PRODUCE THE EXPERIMENTAL RESULTS QUOTED



Source: W.R. Holmes, J.G. Marshall, A.E. Oates, U.S. Patent 3,010,808, November 28, 1961

84.5% w./w. electrolytic hydrogen peroxide containing 0.5 g./l/ of tartrazine was fed in at 490 mls./hr. and cooled to −25°C., at which temperature crystallization occurred. The fraction of feed converted to solid 100% hydrogen peroxide by crystallization was 0.225 by weight. The effective column length was 23 cms.

Washing solution containing 79.8% w./w. hydrogen peroxide at the temperature of operation, and containing no impurity, was added at the rate of 140 mls./hr. The washing ratio was 1.08. The product was run off at 227 mls./hr. and contained 51.4% w./w. of liquor. The tartrazine concentration in the product was 0.009 g./l.

CONTROLLED SELECTIVE OXIDATION OF IMPURITIES BY USE OF A CATALYST COMPRISING A COORDINATION COMPLEX OF A POLYVALENT HEAVY METAL ION WITH TWO DIFFERENT COMPLEXING AGENTS

Shell Oil Co.; Meeker, R.E., and Luten, Jr., D.B. (54): A number of different methods have been suggested for purifying hydrogen peroxide containing organic impurities. Organic impurities more volatile than hydrogen peroxide can usually be efficiently removed by distillation without undue expense. Carboxylic acids are another type of organic impurity which can be removed readily by means of ion exchange resins, preferably anion exchange resins in bicarbonate form. Other organic impurities, and especially those boiling at a higher temperature than hydrogen peroxide, involve greater difficulty in removal without undue loss of peroxide. The method of Dunlop et al claimed in U.S. Patent 2,695,217 employs conversion of the hydrogen peroxide to calcium peroxide as a means for eliminating organic impurities. The process of Pierotti et al (U.S. Patent 2,749,291) makes use of successive evaporations and condensations in combination with steam stripping and recycling operations for removing organic impurities from hydrogen peroxide.

The present process is based upon the discovery that by catalyzing the oxidation of organic impurities in hydrogen peroxide by a coordination complex of a polyvalent heavy metal ion with two different complexing agents, one of which is substantially replaceable by acetate ion and the other of which is not so replaceable, two adjacent coordination sites of the complex catalyst being occupied by the substantially replaceable complexing agent, the desired reaction is promoted without promoting loss of hydrogen peroxide through decomposition; and under the preferred conditions of operation, decomposition is substantially completely avoided.

This was quite unexpected, since the heavy metals are well-known to be very active catalysts of hydrogen peroxide decomposition. It would have been predicted therefore that addition of heavy metal compound of any kind to hydrogen peroxide would be undesirable. However, the special kind of heavy metal compounds indicated above are unique. They not only effectively catalyze the oxidation of organic impurities in hydrogen peroxide without promoting peroxide decomposition, but also promote controlled oxidation of these impurities to carboxylic acids instead of further oxidation products, so that only a very small consumption of peroxide is required for the process.

It may be pointed out that there appears to be a casual relationship between the structure of the coordination compounds used in this process and their unique catalytic activity. The

polyvalent heavy metals are recognized — see, for instance, Stability Constants, Part I: Organic Ligands, by Bjerrum et al — as forming coordination complexes in which there are up to six or more sites for attachment of the complexing agents. The complexing agents here under consideration are the so-called Lewis bases or compounds which tend to donate electrons. In the coordinate complexes used as catalysts in the process, at least one of these sites must be occupied by a base which is relatively difficult to replace with acetate ion, as previously mentioned.

The presence of this difficultly removable base in the complex is believed to be responsible for the suppression of the peroxide decomposing activity of the polyvalent heavy metal used. There is evidence to support the view that the first step in the oxidation of organic impurities in hydrogen peroxide is formation of an organic peroxide. This oxidation, rather than the catalytic step, appears to be the rate-determining step at low pH.

The peroxide is believed to be a hydroxy peroxide which attaches to two adjacent sites of the heavy metal coordinate complex by replacement of the complexing agent or agents which are substantially replaceable by acetate ions and which were attached to those sites in the starting catalyst. The strong attraction of the polyvalent heavy metal in the complex for electrons results in breakage of the peroxide group of the attached hydroxy peroxide with formation of carboxylic acid. The acid molecules thus produced are easily replaced in the complex by new molecules of hydroxy peroxide, and so the catalytic cycle continues.

The process thus comprises adding to aqueous hydrogen peroxide, a coordination complex of a polyvalent heavy metal containing two or more complexing agents having different replaceabilities by acetate ions (at least one of which is not substantially replaceable, while another of the complexing agents is substantially replaceable by acetate ions), there being at least two adjacent coordination sites occupied by the more replaceable complexing agent, and finally removing from the reaction mixture the carboxylic acid formed in the process.

The polyvalent heavy metals which are used in the coordinate complexes employed as catalyst include the recognized heavy metal oxidation catalysts, particularly the metals of the first transition series, namely vanadium, chromium, manganese, iron, cobalt, nickel, and copper, and other transition series metals such as molybdenum, rhodium, tungsten, platinum, mercury, and lead. Suitable compounds which can be used to introduce into the coordination complexes of these metals the necessary ligands which are not substantially replaceable by acetate ions are described in the previously mentioned book of Bjerrum et al.

Amines are one useful type of compound for preparing the coordination compounds employed as catalyst, especially those such as propylenediamine, ethylenediamine, diethylenetriamine, triethylenetetramine, hexamethylenetriamine, phenylenediamine, diaminocyclohexane, aminopyridine, dipyridyl, o-phenanthroline, and the like. The heterocyclic amines such as pyridine, beta-picoline and gamma-picoline, etc. are also useful.

Polycarboxylic acids such as oxalic, maleic, succinic, adipic, citric, tartaric, phthalic, terephthalic, and like acids are another suitable type of chelating agent for use in making catalysts for use in the process. Amino acids can likewise be used, picolinic, alpha-aminopropionic, anthranilic, asparaginic, glutamic, hippuric and quinolic acids, for instance, being suitable examples. The hydroxy acids such as salicylic, for example, are suitable.

An especially advantageous class of compounds that is successfully used in making heavy metal coordinate compounds which are useful catalysts are the ion exchange resins. These may be cation exchange resins of the carboxylic acid or of the sulfonic acid type, or may be those containing both types of acid groups, or may be of the phosphonic acid type. Specific cation exchange resins which have been found to be useful are, for instance, the sulfonic acid type resins exemplified by the sulfonated phenolaldehyde condensation resins such as the phenolic methylene sulfonic resins sold by Rohm and Haas Company under the trade name Amberlite IR-100, Amberlite IR-120 and IR-105, the phenolic methylene sulfonic resin supplied by American Cyanamid Company under the trade name Ionac C-200, and the phenolic methylene sulfonic resins; the carboxylic acid type resins such as the salicylic acid-formaldehyde condensation products typical of which are the cation exchange resins disclosed in U.S. Patent 2,471,818, etc.

Sulfonated cross-linked polymers of polyvinyl aryl compounds such as divinyl benzene or of mixtures of such polyvinyl aryl compounds with monovinyl aryl compounds such as styrene are especially useful in making the coordination compound catalysts for this process, because of their resistance to attack by hydrogen peroxide. Resins of this type are described in U.S. Patent 2,366,007, for instance, and are sold by Dow Chemical Company as Dowex 50. A typical phosphonic acid resin is Duolite C-63, manufactured by the Chemical Process Company. The ion exchange resin may also be an anion exchanger of the weak base type such as Dowex 3, containing free amine functional groups which can hold the heavy metal catalyst ion by forming complex metal-amine bonds.

Suitable complexing agents substantially replaceable by acetate ion include, for example, H_2O, OH^-, Br^-, Cl^-, F^-, $SO_4^=$, NO_3^-, NO_2^-, SCN^-, CH_3COO^-, $HCOO^-$ and the like. Two adjacent sites on the heavy metal ion may be occupied by two of the same or by different substantially replaceable complexing agents. It is not always necessary that the catalyst have the replaceable complexing agents initially on adjacent sites. For example:

$$\text{trans-}[Co(en)_2Cl_2]^+$$

is a suitable catalyst, because in solution it isomerizes to cis-$[Co(en)_2Cl_2]^+$ and hydrolyzes to

$$\text{Cis-}[Co(en)_2ClH_2O]^{++}$$

and to cis-$[Co(en)_2(H_2O)_2]^{+3}$, where the cis-isomers have the chloro or aquo groups in the desired adjacent sites on cobalt.

While all the coordination compounds of the polyvalent heavy metals of the previously indicated characteristics are useful catalysts in the process, all are not equivalent. Thus, it has been found that those made with chromium and/or cobalt and/or copper as the heavy metal are outstandingly superior to the coordinate compounds of the other suitable heavy metals. The compounds made with nickel are excellent, but give slower oxidation rates than the corresponding cobalt complexes. The corresponding complexes of iron, for instance, are generally inferior to those of cobalt because of higher decomposition losses of hydrogen peroxide. In general, the most advantageous catalysts, all things considered, are the

coordinate complexes of cobalt with cation exchange resins of the sulfonic acid type, especially those from sulfonated aromatic hydrocarbon resins.

When using polybasic acids in making the coordinate complex catalysts, it has been found desirable to neutralize any free acid groups remaining in the complex with cations more easily displaced than the polyvalent metal catalyst in the complex. This is especially so when using cation exchange resins in making the catalysts, since the polyvalent metal is seldom able to react with all the acid groups because of steric factors. Cations suitable for this purpose must be inert toward hydrogen peroxide decomposition. Cations which normally exist in solution in only one valence state have been found useful, especially those of the alkali and alkaline earth metals, ammonia and the like.

Catalysts of this preferred type can be readily prepared, for example, by contacting the selected cation exchange resin in the form of its alkali metal or ammonium or alkaline earth metal salt, say the sodium salt form, with an aqueous solution of a salt of the polyvalent heavy metal which has been chosen, for instance, cobalt nitrate. The treatment is continued until the replacement of sodium by cobalt has reached the desired extent, advantageously until the resin is between about 0.1 and about 75% saturated with the chosen polyvalent metal capable of existing in more than one valence state. This catalyst can be used directly in the process.

The process is advantageously carried out at a temperature of the order of about 10° to about 80°C. Operation at about room temperature has the advantage of economy and seems to promote longer effective catalyst life when using coordinate complexes of cation exchange resins, apparently by reducing any attack on the resin by the hydrogen peroxide. Higher temperatures on the other hand promote the desired oxidation and thus reduce the required reaction time and increase plant capacity. Ordinarily a reaction time of the order of about 7 hours at low pH is sufficient to reduce the organic peroxide to about 50%, at or before which point it is desirable to remove the carboxylic acid formed, as will be explained more fully.

It has been found that the desired oxidation can be accomplished in much shorter time by maintaining a pH of about 5.5 to 7 in the reaction mixture. This requires addition of base, preferably an inorganic base such as alkali metal or alkaline earth metal hydroxide, oxide, bicarbonate, ammonia, or the like, sodium hydroxide or lime being particularly suitable because of their cheapness. Operation in this pH range results in two advantages, namely, acceleration of the initial oxidation to the organic peroxide intermediate by hydroxyl ions and promotion of complex formation between the catalyst and the organic peroxide so formed. A pH substantially above 7, which would otherwise be desirable for promoting this noncatalytic step in the oxidation, should preferably not be used because of the tendency toward hydrogen peroxide decomposition under alkaline conditions. By operating in the pH range of about 5.5 to 7, the time for 50% reaction can be reduced from about 7 hours at 60°C to about 10 to 30 minutes at 25°C.

As used here, pH means the pH reading obtained in the usual way with a pH meter and glass-calomel electrodes. In dilute aqueous hydrogen peroxide solutions, this pH reading does not differ substantially from the "true aqueous pH". For peroxide concentrations of about 30% wt. or higher, the difference becomes appreciable, and corrections must be applied, as

described by J.R. Kolczynski et al in the Journal of the American Chemical Society, vol. 79, page 531 (1957).

As previously indicated the carboxylic acid formed in the oxidation is removed from the reaction mixture to obtain the desired hydrogen peroxide of lower organic impurity content. The removal of the carboxylic acid can be carried out in any suitable way. For instance, any of the known methods of removing organic acids from hydrogen peroxide can be employed. Thus steam stripping can be used as, for example, in the method of Pierotti et al (U.S. Patent 2,749,291).

It is a special feature of this process that the carboxylic acid obtained can be removed by means of anion exchange resin. For this purpose, it is desirable to use an anion exchange resin which is resistant to attack by the hydrogen peroxide solution under the conditions used for the purification. It is desirable to employ a strong base resin of the quaternary ammonium salt type as distinguished from the weak base resins (primary, secondary and tertiary amine type resins) normally used for removing unionized acids from aqueous solutions, because carboxylic acid removal is more complete with strong base resin and because weak base resins give too high a pH for peroxide stability.

Examples of strong base resins which are advantageously used in the process are the products of amination with trimethyl amine, for instance, of a chloromethylated styrene-divinyl benzene copolymer as described in U.S. Patent 2,591,573 and sold by Rohm and Haas under the trade names Amberlite IRA-400 and Amberlite IRA-401; anion exchange resins made by the process of U.S. Patent 2,388,235 and the resins sold by Dow Chemical Company under the trade names Dowex 1, Dowex 2, and Dowex 21K or by National Aluminate Corporation under the trade name Nalcit SBR or the like. Duolite A42, A101 and A102, made by Chemical Process Company, Redwood City, California, are other anion exchange resins suitable for use in the process.

The strong base resins are preferably used in the form of their salts rather than in the free base form, especially when they are employed in admixture with the heavy metal coordinate complex catalyst as in a preferred modification of this process. In this way, one avoids the high pH which these resins would otherwise cause and which tends to promote undesirable hydrogen peroxide decomposition, particularly when heavy metals are present. Use of the basic resins in the form of their inorganic salts is usually most advantageous.

The fluoride form is especially efficient for removal of the carboxylic acid but renders the hydrogen peroxide solutions corrosive. There are advantages in using anion exchange resin salts which introduce anions useful in the stabilization of hydrogen peroxide. In this category are, for example, the nitrate salts or more suitably the phosphate or better yet, the pyrophosphate salts. The mono- and/or disodium phosphate salts of Dowex 1 anion exchange resin, for instance, are especially useful in that the sodium acid phosphate introduced into the H_2O_2 by exchange reaction also helps to buffer the peroxide solution at a pH in the desired range of about 5.5 to about 7, without the necessity of adding a full equivalent of caustic. Other inorganic salts of anion exchange resins which can be used include the carbonate or bicarbonate.

The process can be carried out in a number of different ways using batch, intermittent or

continuous methods of reaction. One simple method of batch reaction, for instance, comprises contacting the aqueous hydrogen peroxide to be purified with the chosen heavy metal coordinate complex being employed as catalyst for the required length of time, preferably while adding a base, e.g., NaOH, to maintain the mixture at optimum pH as previously indicated, and then separating the carboxylic acid formed by one of the methods previously described. In this modification of the process, when using catalysts which are solids insoluble in the peroxide solution, the contact of catalyst and solution is usually effected by stirring a slurry of catalyst and solution in a reaction vessel or tank or by pumping this slurry through a coil or a tank provided with baffles or other means to promote intimate contact at a rate sufficient to keep the catalyst uniformly suspended.

Alternatively, the hydrogen peroxide solution to be purified can be passed through a stationary bed of solid, insoluble heavy metal coordinate complex catalyst, this being an especially advantageous method of employing the catalysts made with a cation exchange resin as the coordinating compound.

To minimize hydrogen peroxide decomposition losses, it is advantageous, as previously pointed out, to remove the acid formed in the reaction before too great an amount has accumulated in the reaction mixture, and more advantageously before the oxidation of the organic impurities has reached 10% of completion. It is particularly desirable to remove the acid before the amount present exceeds 0.005 mol per liter of solution. One can, for example, carry out the process continuously in a series of steps in which the hydrogen peroxide to be purified is fed to a first reaction stage in which it is contacted with a slurry of heavy metal coordination complex catalyst, from which it is separated after the desired partial conversion of the organic impurities to carboxylic acid has been completed.

The peroxide solution is then passed through a bed of anion exchange resin to remove the carboxylic acid and subsequently fed to a second reaction stage like the first, where it is again contacted with heavy metal coordination complex of the character previously described. After the second reaction stage, the hydrogen peroxide solution is again passed through a bed of anion exchange resin. Usually two stages of reaction in this way are sufficient to reduce the organic impurities to permissible levels, but three or more stages each with an associated anion exchange resin bed for removing the carboxylic acids formed are sometimes desirable in this modification of the process.

The method of acid removal with a strong base anion exchange resin in bicarbonate form is especially advantageous, particularly when carried out by dispersing the peroxide solution over the bed of anion exchange resin in bicarbonate form by means of an inert gas, preferably a gas containing carbon dioxide sufficient to maintain the pH below about 6.5.

Another especially useful modification of the process makes use of a reaction tank in which the uncatalyzed initial stage of the reaction is permitted to take place with formation of organic peroxide as previously discussed, after which the hydrogen peroxide solution is contacted with a mixture of heavy metal coordination complex oxidation catalyst and anion exchange resin to remove the carboxylic acid produced substantially as fast as it is formed.

Indeed, the use of these mixtures of coordination complex catalyst, especially complexes of heavy metal with cation exchange resins, and anion exchange resin are exceptionally

useful whether or not the separate noncatalytic oxidation step is employed. Most advantageously, these mixtures of catalytic heavy metal on cation exchange resin with anion exchange resin are used in the form of stationary bed through which the peroxide solution is passed either up or downward. When using a bed of this type in combination with the noncatalytic oxidation step previously mentioned, a convenient mode of operation is as follows.

The hydrogen peroxide solution to be purified, with added base for pH control, is fed to a stream of hydrogen peroxide solution flowing from the noncatalytic reactor to the bed of mixed catalyst and anion exchange resin. After passage through this bed, a portion of the solution corresponding in volume to the crude feed is withdrawn as purified product, while the remainder is returned to the noncatalytic reactor for reaction as previously indicated. Still other methods of applying the principles of the process can be employed.

The catalysts used in the process have a long life and generally require no reactivation. However, under certain circumstances they may tend to lose a portion of their catalytic polyvalent heavy metal content after extended periods of use. In such cases, this metal content can be replaced by the procedure used initially in making up the catalyst as previously described. The anion resin used in one of the preferred embodiments of the process for removal of the carboxylic acid or acids formed in the oxidation will usually require regeneration at periodic intervals. The conventional methods of regeneration are usually satisfactory.

TREATMENT WITH ACTIVATED CHARCOAL SLURRY UNDER NONALKALINE CONDITIONS

Du Pont; Elston, A.A., and Hinegardner, W.S. (55): Purification in this process is accomplished by intimately contacting an aqueous hydrogen peroxide solution with a finely divided activated carbon under agitation and under nonalkaline conditions, to effect adsorption of impurities on the activated carbon; and then separating the latter from the solution before any substantial peptization of the activated carbon in the solution occurs.

The activated carbon employed should be one which gives a slurry having a pH not exceeding 8, preferably less than 7, when slurried with carbon dioxide-free distilled water at a carbon concentration of 1% by weight of the slurry. Most preferably, the pH will be in the range 4.5 to 6, but activated carbons more acidic can be used. Also, the activated carbon should be one which will not cause excessive decomposition of the peroxide under the conditions of use.

Activated carbons have long been regarded as active peroxide decomposition catalysts, and it would have been expected that a more highly activated carbon would decompose hydrogen peroxide more rapidly than a less highly activated carbon. It has now been found, however, that this is not necessarily the case and that some of the most highly activated commercial carbons are best suited for the purpose and result in insignificant peroxide decomposition when employed under proper conditions. Ordinarily, use of the activated carbon should not result in decomposition of more than about 2% of the peroxide being treated, although somewhat higher losses may be tolerable in some cases. Preferably, the loss will not exceed about 0.5%.

It has been found that the peroxide decomposition loss due to contact with an activated carbon is less when using the carbon in a finely divided form than when using it in a coarse or granular form. Thus, an activated carbon which effectively removes organic impurities by this method with relatively little peroxide decomposition when the carbon is used in finely divided form, causes such high peroxide losses when the carbon is in a coarse or granular form as to make use of the latter entirely impractical or even dangerous.

Ordinarily, the activated carbon should be substantially free of particles larger than about 50 mesh. Preferably, the particles will be as finely divided as possible, while still permitting their rapid and complete separation from the treated solution by filtration or equivalent methods. Particles of sizes ranging from 100 to 325 mesh (Tyler standard sieve) or finer are generally suitable. Use of an inert filter aid along with the activated carbon may permit employing the latter in a more finely divided form than would otherwise be practical.

The preferred activated carbons are the commercially available, finely divided, activated, acid treated, and washed, activated carbons derived from wood or wood products such as sawdust, or from the residues of wood pulping waste liquors, e.g., sulfite process liquors. Other highly activated carbons which do not cause excessive peroxide decomposition can be used.

The treatment of the peroxide solution with the activated carbon should be effected under agitation and under nonalkaline conditions, i.e., the mixture of the solution and the carbon should be agitated and should have a pH not greater than 7. Preferably, the pH of the mixture will not differ by more than 2 pH units (either above or below) from that pH which corresponds to the equivalence point (as defined in U.S. Patent 2,497,814) of a pure aqueous solution of the same H_2O_2 concentration, since these conditions minimize peroxide decomposition and enhance adsorption of the organic impurities. Most preferably, the pH will be within 1 pH unit of the pH representing the equivalence point. More acidic conditions can also be used but usually offer no added advantages.

The time of contact between the finely divided activated carbon and the peroxide solution is important. Some activated carbons adsorb the organic impurities very rapidly, with maximum adsorption being reached within 1 to 4 minutes. Others having substantially the same adsorption capacity for the impurities require more than an hour to reach maximum adsorption. It has been found that the optimum contact time is substantially the time required to achieve maximum adsorption of the impurities. Since this time varies widely for different activated carbons, the optimum time for any given carbon must be determined by actual test.

Contact between the activated carbon and the peroxide solutions for a time longer than about 2 to 3 times that required to achieve maximum adsorption of impurities should be avoided, particularly when treating relatively concentrated peroxide solutions, e.g., solutions of greater than about 20% strength. It has been found that if a longer contact time is employed, such peroxide solutions actively peptize the carbon particles to give colloidal carbon particles which are difficult to separate completely from the solution.

Furthermore, the adsorbed organic impurities tend to become desorbed during such peptization, so that the total carbon content (including colloidal carbon) of a solution which has been in contact too long with the activated carbon may exceed that of the original solution.

Fortunately, it has been found that such undesirable peptizing action can be substantially completely avoided by avoiding contact times substantially longer than 2 to 3 times that required for maximum adsorption of impurities. Peptization does not occur to any substantial extent until after maximum impurity adsorption results. It is, therefore, desirable that the activated carbon is rapidly and completely separated from the solution as soon as maximum adsorption has been reached.

The amount of any given activated carbon to be used will depend chiefly upon its adsorptive capacity, the amount of impurities in the solution to be treated, the degree of purification desired, and the time and temperature of the treatment. Generally, the amount will range from about 0.1 to 1.0%. For any given activated carbon, the concentration of organic impurities remaining in the treated solution appears to vary inversely and linearly with the logarithm of the amount of activated carbon used over the range up to about 1% of the latter. Multiple treatments with the activated carbon may be desirable when treating solutions containing relatively high concentrations of impurities, or when a product especially low in organic impurities is desired.

It is generally desirable to control the temperature of the activated carbon solution mixture during the treatment, since both adsorption of the impurities and decomposition of the peroxide are influence by temperature. Temperatures above about 40°C. are best avoided to prevent excessive peroxide decomposition. Temperatures not higher than 35°C. are preferred. The most suitable temperatures range from about 21° to 30°C. Temperatures considerably below about 21°C. can be used, but are not preferred since they reduce substantially the rate of adsorption of the organic impurities. Optimum balance between the stability of the peroxide solution and the rate of impurity adsorption generally will occur at temperatures within the range of about 21° to 30°C.

The process is illustrated by the following example. All values expressed as parts per million (ppm) are based upon the weight of the peroxide solution.

The solution treated was an impure aqueous solution containing 35% H_2O_2 and organic impurities equal to 120 ppm, calculated as carbon. It had a pH in the range 2.0 to 2.5, a slightly yellow tint, a slightly organic odor, and a surface tension of 67.4 dynes/cm. (as compared with values of 73.2 and 72.0 dynes/cm., respectively, for a pure aqueous solution of the same hydrogen peroxide concentration and for pure water). The organic impurities consisted chiefly of aliphatic carbonyl and carboxyl compounds, and hydroperoxides of up to 9 carbon atoms, with traces of aromatic compounds.

The activated adsorbent carbon selected for treating the above solution was a finely divided (about 100 to 300 mesh), bulky, relatively soft, acid treated, washed, commercial activated carbon prepared from the residue of sulfite waste liquor obtained in the manufacture of sulfite wood pulp. A 1% slurry of the carbon in carbon dioxide-free distilled water had a pH of about 5.6. In a preliminary test of the carbon, it was found that the peroxide decomposition loss, when 0.5 g. of the carbon was suspended under agitation in 100 ml. of the peroxide solution for 5 minutes at room temperature, did not exceed 0.4% of the hydrogen peroxide originally present.

One part of the above activated carbon was slurried with 200 parts by weight of the above

peroxide solution. The slurry was agitated for 5 minutes at room temperature (24° to 26°C.), then rapidly filtered through a fine filter medium with the aid of vacuum. The H_2O_2 content of the filtered solution was about 34.86%. It contained organic impurities equivalent to only 10 ppm of carbon, representing an organic impurity reduction of 92%. It was clear, colorless and odorless and its surface tension was 73.7 dynes/cm.

DECOLORIZING PROCESS COMPRISING SOLVENT EXTRACTION, HEATING IN DIGESTION ZONE, AND DISTILLATION

FMC Corp.; Siwinski, G.W. (56): While the anthraquinone process is desirable for economic and other reasons, the hydrogen peroxide which is produced by it characteristically contains organic impurities such as entrained working solution, dissolved anthraquinones, and anthraquinone degradation products. These impurities tend to impart an undesirable color to the peroxide product. This color renders the peroxide unsuited to applications which require the use of substantially color-free hydrogen peroxide, for example, the preparation of epoxy-containing plasticizers, cosmetic products, and the like.

Heretofore, a conventional method for removing impurities from aqueous hydrogen peroxide produced by the anthraquinone process has been to pass the aqueous solution of hydrogen peroxide through a series of washing or extracting elements, known in the art as decolorizers, and then to recover and distill the peroxide solution. These decolorizers are packed columns in which the aqueous hydrogen peroxide is contacted with a solvent which is useful in dissolving alkylated anthraquinones. Solvents of this type are referred to in the art as quinone solvents; typical quinone solvents have been described in U.S. Patents 2,768,065 and 2,768,066. Other purification systems employing adsorbing solids such as solid polyethylene in place of the decolorizers are also known. Such units also remove substantial amounts of organic impurities from the aqueous hydrogen peroxide solution, and are followed by a distillation to further purify and concentrate the hydrogen peroxide.

While such purification methods produce substantially water-white hydrogen peroxide, the product on prolonged storage develops an undesirable color which becomes increasingly deeper as the storage time increases. This results in a competitive disadvantage for anthraquinone-produced hydrogen peroxide versus hydrogen peroxide produced by the electrolytic method. Repeated extractions and distillations have not eliminated this coloring of anthraquinone-process hydrogen peroxide upon standing.

It has now been found that color-forming impurities can be removed in one rapid operation by inserting intermediate the primary separation step and the final distillation, the step of heating the primarily-treated hydrogen peroxide in the presence of a stabilizer for a period of time which is short relative to the time required for discoloration in storage, yet suffices to convert the impurities into forms which can be removed by conventional means; this heating step can be carried out without any substantial loss of hydrogen peroxide. It has further been determined that the resultant conversion products of the impurities can only be removed from the hydrogen peroxide by a separate, solvent extraction step succeeding this heating step and followed by a final distillation.

More specifically, the preferred embodiment of this process comprises initially solvent

extracting the aqueous hydrogen peroxide to remove entrained working solution; heating the resultant raffinate in the presence of a stabilizer until it becomes sufficiently colored to indicate the conversion of the color-forming impurities into other forms; solvent extracting the digested solution to remove part of the converted impurities; distilling the resulting raffinate to remove volatiles and the remaining converted impurities; and recovering the purified hydrogen peroxide solution as bottoms.

The changes in color of anthraquinone-process hydrogen peroxide are believed to be due to colorless organic materials which remain in the peroxide following the extraction step; these materials remain in the hydrogen peroxide even after distillation, and revert in progressive stages to colored impurities upon prolonged storage. However, upon being treated in the present heating (digestion) operation, they are converted into a form in which they can be separated from the hydrogen peroxide by solvent extraction and distillation. These particular organic materials are believed to be quinones which are either hydrolyzed or oxidized, and other degradation products of anthraquinone. However, regardless of the accuracy of this understanding, this treatment of aqueous hydrogen peroxide from the anthraquinone process provides a hydrogen peroxide product having substantially no color and which remains substantially free of color upon aging.

In the broad concept of the process, purification of aqueous hydrogen peroxide solution produced by the anthraquinone process is accomplished by initially separating the aqueous hydrogen peroxide from the organic impurities using solvent extraction, adsorbing beds, or other equivalent means, heating the residual peroxide solution in a digestion zone to a temperature of about 150° to 50°C. for about 1 to 10 hours to effect the desired conversion, subsequently extracting the treated solution with a quinone solvent in a secondary extraction zone at a temperature of about 10° to 60°C., and finally distilling the treated hydrogen peroxide solution. The recovered aqueous hydrogen peroxide solution is substantially free of color, and remains substantially color-free upon prolonged storage. Anthraquinone-process hydrogen peroxide purified by this process is competitive in color with peroxide produced by prior art electrolytic methods, and finds application in processes and products in which color is an important consideration.

The starting material is a crude aqueous hydrogen peroxide, typically containing about 10 to 30% weight of hydrogen peroxide in water, which is obtained from the conventional anthraquinone process. In a preferred embodiment of the process, this solution is first extracted with a quinone solvent in a primary extraction zone which comprises from one to four, and preferably from two to four, extraction towers connected in series and maintained at a temperature of about 10° to about 60°C. The contact time between the aqueous hydrogen peroxide and the quinone solvent in the extraction zone may vary from 0.1 to 10 hours.

One important factor is that the contact time should be sufficient to assure efficient mass transfer between the peroxide solution and the quinone solvent. Thus, the time of contact is dependent on the amount and efficiency of the packing used in the extraction equipment. Additionally, for a given extraction system, there is an inverse relationship between time and temperature, with times near the lower end of the above time range being suitable when the operation is conducted at a temperature approaching 60°C., and times near the upper end of the above time range being desirable when the operation is conducted at temperatures approaching 10°C.

The extraction towers, which comprise the extraction zone, are suitably packed towers providing good mass transfer between the aqueous solution of hydrogen peroxide and the quinone solvent. The aqueous hydrogen peroxide solution is recovered as raffinate free of residual alkylated anthraquinone and any other portions of the work solution initially entrained in the aqueous hydrogen peroxide. The recovered raffinate has an anthraquinone concentration below 10 parts per million; this represents a removal of over 90% of the anthraquinone present in the crude aqueous hydrogen peroxide solution. The recovered raffinate likewise has a reduced color value; namely, on the order of about 2 on the ferric chloride scale.

The ferric chloride scale is a color index used to indicate the color of the peroxide solution. The solution is visually compared with a series of standard ferric chloride solutions in standard 50 ml. tall form Nessler tubes. The solutions are made up by adding quantities of a 1/6 molar ferric chloride ($FeCl_3.6H_2O$) solution into 50 ml. Nessler tubes and diluting with water to 50 ml.; they are numbered from 0 to 10, with the lower numbered solution being lighter color. The solution numbered 0 is made up by adding 0.1 ml. of the 1/6 molar ferric chloride solution, and 0.2 ml. increments are added for each succeeding higher numbered solution. Thus solution 10 ultimately contains 2.1 ml. of the 1/6 molar ferric chloride solution diluted with water to 50 ml.

The aqueous hydrogen peroxide raffinate obtained from the primary extraction zone is then heated in a digestion zone. The digestion step comprises maintaining the solution at a temperature of about 150° to 50°C., and preferably about 100° to 80°C., for a time sufficient to obtain the desired color conversion in the solution, usually about 1 to 10 hours. The digestion step converts color formers, which are virtually colorless organic impurities in the peroxide obtained from the anthraquinone process and which are not removed by simple extraction and distillation, to either alkylated anthraquinones or to other colored impurities. That is, the color formers are either converted to relatively nonvolatile colored impurities, or are converted back to the original alkylated anthraquinone.

In any event, the digestion converts substantially all of the color formers in solution to other materials. During the digestion operation the color of the peroxide solution is substantially increased, preferably to its maximum color value of about 6 to 10 on the ferric chloride scale; and the digestion is preferably controlled by determining this increase in color, since it indicates when complete conversion of the color-forming impurities has occureed.

The aqueous hydrogen peroxide solution, which now contains anthraquinones and other colored impurities, is treated in a second extraction zone. The conditions under which this operation is conducted are preferably those recited for operation of the primary extraction zone, although the two steps need not be conducted under the same conditions in a given purification operation. The quinone solvent employed in the extraction removes the newly formed alkylated anthraquinone. The raffinate peroxide solution, which is now free of anthraquinone, is then passed into a fractionator, where pure aqueous peroxide is separated from the relatively nonvolatile colored impurities.

The resulting peroxide product has a color value of close to 0 on the ferric chloride scale, and does not increase above a value of about 0.5 when heated or upon prolonged storage. This color is too faint to be observable by the naked eye, and is of the same order of magnitude as that of electrolytically-produced hydrogen peroxide, which reaches a maximum

value of about 0 to 1. The quinone solvents which are suitable as extracting media in the extraction zones include toluene, alkylated naphthalene, mixtures of alkylated naphthalenes and paraffins, chlorinated aromatics such as dichlorobenzene and trichlorobenzene, chlorinated alkanes, e.g., trichloromethane, tetrachloromethane, dichloromethane, and trichloroethane.

The primary and secondary extraction zones operate at atmospheric, or superatmospheric pressures. However, operation at atmospheric pressure is preferred. The digestion may be operated at either subatmospheric, superatmospheric, or atmospheric pressure. However, open vessels operating at atmospheric pressure are preferred for the digestion operation.

It has been found that when the digestion operation is conducted at temperatures near the upper end of the temperature range, and for long times, substantial amounts of hydrogen peroxide may be decomposed. Since it is desirable to hold the decomposition of peroxide to a minimum, it has been found advantageous to employ a typical stabilizer for hydrogen peroxide such as sodium stannate, dipicolinic acid, and the like, in amounts of 1 to 10 parts per million during the digestion.

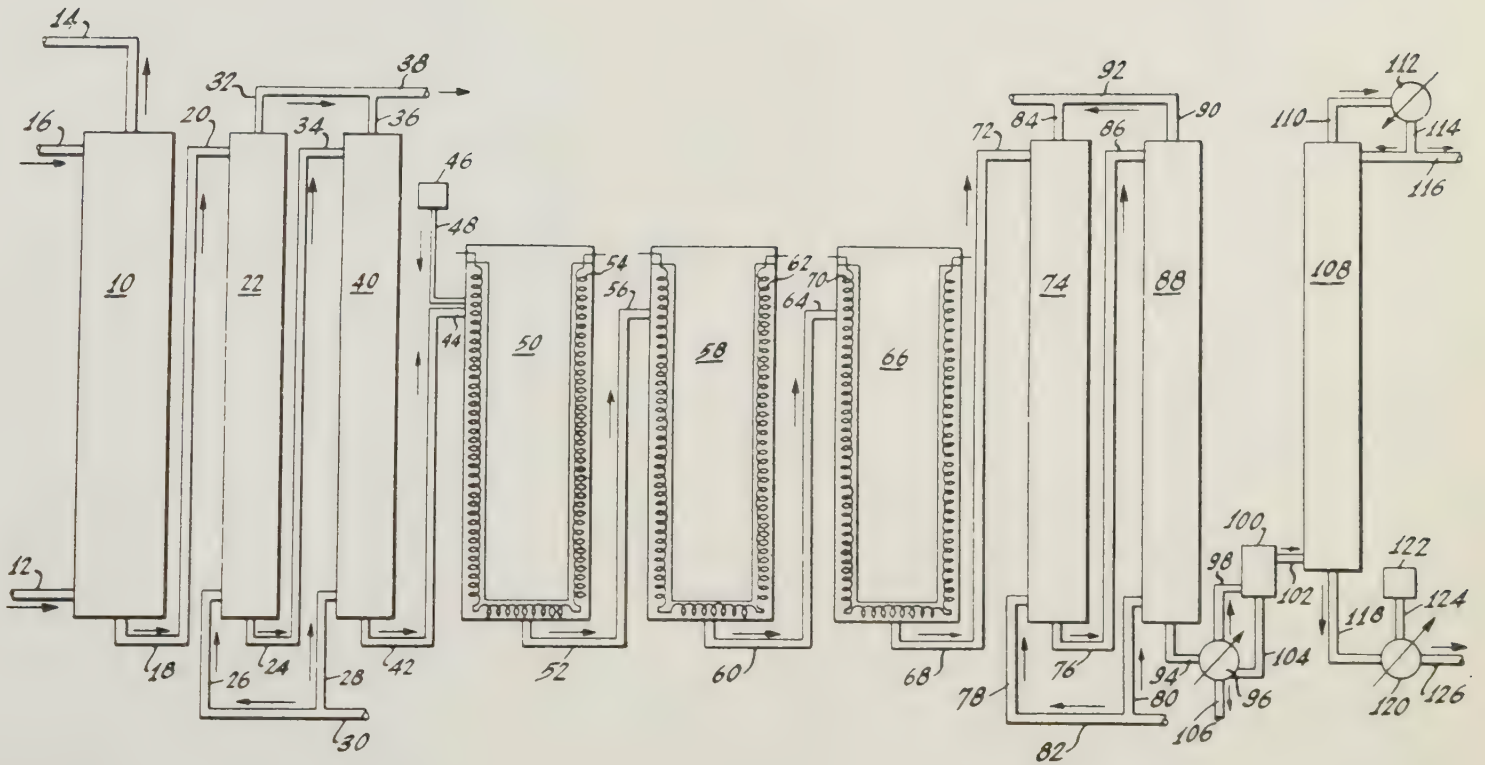
This stabilizer holds the decomposition of the product to a minimum, usually to less than 1% to 5%. In this connection, if the digestion step is permitted to proceed for a period beyond the point of maximum color formation, particularly without a stabilizer, the colored impurities will react with peroxide resulting in peroxide losses of up to about 25%. However, when a stabilizer of the above type is employed, and the period of digestion is controlled so that maximum color is produced without excessive digestion, peroxide losses normally are maintained at less than about 5% of the total peroxide present.

It has further been found that if the purified hydrogen peroxide solution is desired in a particularly color-free condition, and must remain so upon standing, completely color-free peroxide may be obtained by heating the purified solution of aqueous hydrogen peroxide for a period of about 30 minutes at about 100°C. following the fractionization operation. This additional treatment preferably is performed in the presence of a stabilizer such as the above mentioned sodium stannate stabilizer, in concentrations of about 1 to 10 parts per million. Alternately, treatment for as long as 1 hour at a temperature as low as about 70°C. has been found effective in removing the final traces of color and potential color from the hydrogen peroxide. The added stabilizer prevents substantial destruction of hydrogen peroxide during this additional treatment.

The process will now be described with reference to Figure 4.3, which is a schematic flowsheet. A working solution of anthraquinone and hydrogen peroxide enters peroxide removal tower 10 through line 12, while water enters the top of the tower through 16. The aqueous extract of hydrogen peroxide is removed through line 18 and passed into primary extractor 22. The working solution, substantially free of hydrogen peroxide, is removed from tower 10 through overhead line 14 and recycled back to the anthraquinone hydrogenator, not shown. A quinone solvent enters primary extractors 22 and 40 through lines 30, 26 and 28, and extracts anthraquinone from the peroxide solution. Columns 22 and 40 are primary extraction towers having conventional packing.

If desired, the quinone solvent may be passed through the extractors in series rather than in

FIGURE 4.3: FLOWSHEET OF THE FMC HYDROGEN PEROXIDE PURIFICATION PROCESS



Source: G.W. Siwinski, U.S. Patent 3,043,666, July 10, 1962

parallel flow as shown. The extract phases of primary extractors 22 and 40 are removed through line 38 from lines 32 and 36. The hydrogen peroxide raffinate from extractor 22 passes into extractor 40 through lines 24 and 34, for an additional extraction step. Additional primary extractors may be employed, if desired, The raffinate from extractor 40 then enters digester 50 through lines 42 and 44.

The aqueous peroxide solution, which is substantially free of alkylated anthraquinone, is heated in digester 50 by heating means 54. A stabilizer is added to the hydrogen peroxide solution in digester 50, from container 46 through line 48. The hydrogen peroxide solution is then passed in series through lines 52 and 56 to digester 58, then through lines 60, 64 into digester 66, each of these digesters having heating means 62 and 70 respectively. Additional digesters may be employed, but three have been found sufficient to prevent any undesirable backmixing. If less than three digesters are used, backmixing hampers efficient digestion. The peroxide solution is preferably held in the digesters until it reaches its maximum color in the last digester 66, indicating complete conversion of the color-forming impurities.

The digested peroxide solution, by virtue of the digestion step, is purified of color formers, leaving anthraquinone and colored impurities as the remaining contaminants. This solution is then passed from digester 66 to a secondary extractor 74 through lines 68 and 72, and subsequently to another secondary extractor 88 through lines 76 and 86. These secondary columns 74 and 88 are extraction columns of the same kind as the primary extraction towers. Two or more extraction towers may be employed in this secondary extraction step. A quinone solvent flows into extractors 74 and 88 through lines 78, 80 and 82, in the same manner as the primary digesters.

The raffinate from secondary extractor 88 then enters heater 96 through line 94. The hydrogen peroxide, water and other volatiles are vaporized in heater 96, and flow through line 98 into a separating zone 100. Entrained nonvolatiles are separated in zone 100, and returned to heater 96 through line 104. Relatively high boiling compounds such as colored impurities are removed through line 106 from heater 96. The volatile compounds pass from separator 100 to a fractionator 108 through line 102. This fractionator may be packed with any conventional separating devices, i.e., bubble plates or packing. In the fractionator 108, an aqueous hydrogen peroxide solution is recovered as residue from line 118, while some water and low boilers are removed overhead through lines 110, 114, and 116, after being condensed in cooler 112.

When it is required that hydrogen peroxide should be particularly color-free, even upon prolonged storage, the final traces of color and potential color may be removed by additionally purifying the recovered hydrogen peroxide from fractionator 108 in heating chamber 120. The purified hydrogen peroxide from fractionator 108 is introduced by line 118 into heating chamber 120. A stabilizer is added during this treatment from container 122, through line 124 into chamber 120. The additionally treated hydrogen peroxide is then removed as finished product through outlet 126.

CONTACTING WITH ANION AND CATION EXCHANGE RESINS FOLLOWED BY HEAT TREATMENT

Shell Oil Co.; Meeker, R.E., Dunlop, A.K., and Luten, Jr., D.B. (57): It has been discovered that there is a synergistic or joint catalytic effect between carboxylic acids and heavy metal ions in promoting decomposition of hydrogen peroxide. In the production of hydrogen peroxide from organic sources, crude peroxide containing both of these types of impurities is always encountered at some stage of manufacture. The carboxylic acids, if not originally present in the peroxide, are formed when the peroxide is exposed to elevated temperatures as in evaporation or the like. Due to the corrosive action of hydrogen peroxide on the metal containers in which it is stored on a commercial scale, heavy metal ions are present even when the greatest efforts are made to reduce their amount to a minimum.

One of the methods in use to reduce the undesirable effect of these heavy metal ions in hydrogen peroxide is addition of peroxide stabilizers which form complexes with these ions. Since the bulk of the metal ions often exists as anionic complexes with the added stabilizers, such hydrogen peroxide will contain significant amounts of heavy metal even after treatment with cation exchange resins. This heavy metal content and the carboxylic acid products of oxidation of organic impurities synergistically promote hydrogen peroxide decomposition. The joint catalysis greatly exceeds the sum of the effects of the heavy metal and carboxylic acid. The synergism is shown by the following results of tests with electrolytic hydrogen peroxide diluted to 30% w.

Contaminant added:	Decomposition of H_2O_2 Percent/hr. at 80° C.
0.2 N HCOOH	0.75
0.2 mg./l. Fe	1.8
0.2 N HCOOH + 0.2 mg./l. Fe	10.4

The magnitude of this synergism can be reduced somwhat by pH control but the undesirable peroxide decomposition cannot be avoided completely by attempted removal of the carboxylic acid, because the synergism continues during generation of carboxylic acid by oxidation of the organic impurities present. As a result hydrogen peroxide losses in the prior methods of purification have been greater than is desirable in plant scale operations.

It has now been found that losses of hydrogen peroxide by synergistic catalysis of its decomposition by heavy metals and carboxylic acids during removal of relatively nonvolatile organic impurities by thermal degradation to carboxylic acids which can be subsequently separated from the peroxide, can be minimized by subjecting the impure hydrogen peroxide to treatment to remove both metal cations and heavy metals complexed as anions before carrying out the thermal degradation to carboxylic acids. The process thus has as an essential feature the combination of treatment of hydrogen peroxide containing organic impurities, especially relatively nonvolatile organic impurities, with anion and cation exchange resins to remove heavy metal and then heating the hydrogen peroxide before exposing it to recontamination with heavy metal, the heating being controlled so as to convert relatively nonvolatile organic impurity to carboxylic acids. The acid thus formed is then separated from the hydrogen peroxide.

The treatment with anion and cation exchange resins to remove both the heavy metal cations and complexed heavy metal in anionic form can be carried out in a number of different ways. One advantageous method is to pass the impure hydrogen peroxides through a single bed of mixed anion and cation exchange resins or through successive beds of the two different kinds of resins. The flow may be through separate columns of anion exchange resin and cation exchange resin bed in either order. However, there has been found, unexpectedly, to be a substantial increase in overall resin life by placing the anion exchange bed first in the sequence, since attack of hydrogen peroxide on the cation exchange resin is thus reduced.

A large number of suitable anion and cation exchange resins are available. As a class these resins are high molecular weight polyacids or polybases which are virtually insoluble in, and inert to, the hydrogen peroxide solution being purified. They preferably consist of a three-dimensional hydrocarbon network to which are attached the acid or basic groups which act as the ion exchangers.

The cation exchangers can contain sulfonic, phosphonic, phosphonous, arsenic and like acid groups. Strongly acidic cation exchangers such as sulfonated cross-linked polystyrene are especially advantageous. Examples of these cation exchangers are Amberlite IR-120 produced by Rohm and Haas Company, Chempro C-20 and Duolite C-25 of Chemical Process Company, Dowex 50 of Dow Chemical Company, Nalcite HCR of National Aluminate Corporation and Permutit Q of Permutit Company. Sulfonated phenol-aldehyde condensation products are another form of suitable cation exchange resin which can be used in this process. The sulfonic acid group in these resins can be on a chain, as in a $-CH_2SO_3H$ group, or can be attached directly to the aromatic nucleus.

The first named type is made, for example, by heating together phenol, formaldehyde, and a mixture of sodium sulfite and metabisulfite, then adding more phenol and formaldehyde and heating to gelation, or is made by introducing the sulfonic groups into a preformed phenol-formaldehyde condensate. The second type can be prepared by reacting a paraphenol sulfonic acid with formaldehyde and phenol and heating the resin in drying pans to remove the excess water and form a cross-linkage. This resin has both $-SO_3H$ and $-OH$ groups attached to an aromatic ring, the $-SO_3H$ groups being effective in ion exchange. U.S. Patent 2,676,923 describes nuclear sulfonated aromatic hydrocarbon cation exchange resins which are especially preferred in this process. The patent also shows suitable methods for contacting the resin with the H_2O_2 solution to be purified and for regenerating the resin after use.

While the cation exchange resin can be used in the hydrogen form in the conventional way, there are special advantages in using these resins in the form of salts because the resin is more resistant to attack by the peroxide when in salt form. The cations used in making the resin salts should be such as are not detrimental in the peroxide. Suitable resin salts are, for example, the alkali, ammonium and alkaline earth metal salts. Sodium salts are especially suitable because of their economy and effectiveness.

The preferred anion exchange resins are strong base resins. Especially suitable anion exchange resins of this kind are, for instance, the quaternary ammonium salt type resins, such, for example, as the products of amination with trimethyl amine or dimethyl ethanol amine of chloromethylated polymers, e.g., chloromethylated styrene divinyl benzene copolymers.

Representative commercially available exchangers of these types are Amberlite IRA-400, IRA-401 and IRA-410 of Rohm and Haas Company, Dowex 1 and Dowex 2 of Dow Chemical Company, Nalcite SBR and SAR of National Aluminate Corp., Permutit S-2 of Permutit Co., and Duolite A-42 and A-40 of Chemical Process Co. U.S. Patents 2,388,235 and 2,591,573 describe processes for producing anion exchange resins which can be used in the process.

The chosen anion exchange resin should be used in a salt form to avoid high pH. In this way the undesirable decomposition of peroxide which takes place at high pH, especially in the presence of heavy metal ions, is avoided. Another advantage of using the anion exchange resin in salt form is the greater resistance to attack by hydrogen peroxide which the resins have when used as salts as compared with the resin in hydroxide form. A variety of different kinds of anions can be used in making anion exchange resin salts useful in the process.

A special feature of the process is the use of anion exchange resins in the form of their salts of strong acids for the removal of metal ions complexed as anions from mixtures of these ions with carboxylic acids. It has been discovered that the complexed metal anions can be selectively removed in this way without substantial removal of carboxylic acid. This unexpected improvement has other advantageous applications than in this process, but is especially useful in this new method of hydrogen peroxide purification.

By employing as the anion of the exchange resin salt, an anion of an acid which is stronger than the carboxylic acid in the hydrogen peroxide, catalytic metal ions can be removed from the peroxide without removing carboxylic acid at the same time. The capacity of the resin for metal removal is thus increased compared with operation so as to simultaneously remove carboxylic acid which would require regeneration upon breakthrough of carboxylic acid. Indeed, by using anion exchange resin salts which do not remove carboxylic acid from the peroxide, the capacity of the resin for metal anion removal is so great that as a general rule it is economically feasible to discard it when it has reached saturation rather than to regenerate it for reuse in the process, although regeneration can be carried out simply as described subsequently.

By the use of anion exchange resin salts of strong acids, the desired low pH is maintained in the hydrogen peroxide during complexed metal anion removal without need for exacting control. This makes the operation simpler and more convenient than when resort is had to the bicarbonate salt form of the resin. This can also be used to avoid high pH, but requires vigilance and care in applying the necessary carbon dioxide pressure to insure that localized regions of high pH do not develop. These not only result in undesirable loss of hydrogen peroxide which may lead to a rather rapid pressure rise, but also cause degradation of the resins. All these disadvantages are eliminated by use of strong acid salts of the anion exchange resins.

A number of different anions of strong acids can be used in making the preferred anion exchange resin salts employed in removal of complexed metal anions prior to heat treatment according to this process. Among the suitable anions of acids stronger than the monocarboxylic acid impurities, are, for instance, the nitrate, the sulfate, the hydrogen sulfate, the dihydrogen phosphate, the di- or tri-hydrogen pyrophosphate, the perchlorate, and the like. Fluorides, etc., are also effective but are less desirable because of the corrosion which they promote.

There are special advantages in using salts of strong base anion exchange resins which introduce into the peroxide solution, as a result of the exchange with the metal anions, anions which are useful in inhibiting corrosion or in the stabilization of hydrogen peroxide. In this category are, for example, the nitrate salts which provide a corrosion inhibitor for the peroxide, and the phosphate, pyrophosphate and 1,2-diaminocyclohexane-N,N'-tetraacetic acid salts in their partly protonated forms, which introduce useful hydrogen peroxide stabilizers.

Still other forms of anion exchange resin salts can be used in the process. Salts of the carboxylic acids in the hydrogen peroxide being treated are one suitable form of resin salt, since they do not introduce into the peroxide any undesirable components not already present and at the same time avoid the undesirable high pH of the hydroxyl form of the resin. The acetate and formate salts are convenient salts of this type which can be used successfully.

Whatever the form of anion and cation exchange resins chosen, it is desirable that they be kept below about 80°C. and more advantageously below 40°C. during the contacting, since the life of the ion exchange resins decreases as the contacting temperature increases. The preferred temperature is between about 10° and about 25°C.

The time of contact of the hydrogen peroxide solution with the ion exchange resins can vary widely. Excessively long times of contact which lead to undesirably short resin life per volume of hydrogen peroxide treated due to attack on the resin by the peroxide are of course to be avoided, especially since relatively short times of contact are sufficient to secure adequate removal of heavy metal impurities. Thus times of the order of about 1 sec. to about 1 hour are suitable, and more preferably times of about 10 sec. to about 10 minutes are used.

The removal of heavy metals from the hydrogen peroxide can be effected essentially quantitatively in this way. A high degree of utilization of resin capacity can be realized before breakthrough of heavy metals in either cationic form or as anionic complexes. If desired, regeneration of the cation exchange resin after it has reached the predetermined degree of saturation decided upon can be effected, for example, by treatment with a strong acid or salt such as sulfuric, phosphoric, or nitric acid or sodium nitrate. Acid or salt concentrations of the order of about 2 to 20% by weight, for example, are useful. A convenient way of carrying out the regeneration is to pass the regenerant through a fixed bed of the resin until the effluent shows a negative test for iron by the potassium thiocyanate method. Preferably, the regenerated resin is washed with water to free it of excess regenerant before being used. Thus, in the preferred method, the resin which has been conditioned with sodium sulfate is washed with water until the washings are substantially free of sulfate ion, so that the purified peroxide will not be unduly contaminated with sulfate. The regenerated resins can then be reused in the process.

When the anion exchange resin used for removal of complexed heavy metal from the hydrogen peroxide, before heat treatment to convert organic impurities to a more readily removable form, is to be regenerated instead of replaced with fresh resin, the regeneration can be effected in a number of different ways. Treatment with an appropriate acid or with a suitable salt are suitable methods of regeneration, for example. By these methods of treatment the complexed heavy metal anions can be replaced and the salt form of the anion exchange resin can be simultaneously regenerated for reuse in the process. As in the regeneration of the

cation exchange resin, it is desirable to remove excess regenerating solution from the anion exchange resin by water washing before returning the regenerated resin to the operating cycle in order that unnecessary contamination of the hydrogen peroxide under treatment may be avoided.

A mixed bed of anion and cation exchange resins can be regenerated in situ without separating the two resins, by passing the desired acid over both resins; e.g., HNO_3 regenerates the cation resin in H^+ form and the anion resin in NO_3^- form directly. By the use of a salt for regeneration of the mixed bed, e.g., $NaNO_3$, the cation exchange resin can be obtained in a desirable salt form, while the acid salt of the anion exchange resin is simultaneously regenerated.

After treatment of the hydrogen peroxide with anion and cation exchange resin, the peroxide essentially free from heavy metal is subjected to controlled heat treatment to convert the organic impurity present to a more readily removable form. This treatment essentially consists of thermal degradation of organic impurity in hydrogen peroxide at elevated temperature without added catalyst. In this heating the organic impurity is converted to carboxylic acids, usually predominantly formic and acetic acids. Because of the previous deionization of the peroxide, the degradation of organic impurities can be carried out successfully at high temperatures, at which rapid rates of oxidation of the organic impurity to these more readily removable acids takes place with minimized peroxide loss.

It has been found that within the temperature range of about 60° to about 200°C., the rate of degradation of organic impurities in hydrogen peroxide increases much more rapidly with temperature when the peroxide has been deionized than is the case with nondeionized peroxide. The rate of hydrogen peroxide decomposition, on the other hand, increases much more rapidly with temperature for crude nondeionized hydrogen peroxide than for the same peroxide deionized. The comparative activation energies for these different reactions are approximately as follows:

	Organic Impurity Decomposition, E_1 (kcal. per mole)	Hydrogen Peroxide Decomposition, E_2 (kcal. per mole)	E_1-E_2
Non-deionized Hydrogen Peroxide	14	26	−12
Deionized Hydrogen Peroxide	21	16	+5

The surprising change in sign of the activation energy difference, upon which the selectivity of the thermal degradation of the organic impurities depends, explains the success of high temperature treatment in this process as contrasted with earlier results with hydrogen peroxide which had not been treated with both anion and cation exchange resins to remove both anionic and cationic forms of heavy metal before heating.

Temperatures of thermal degradation of about 110° to about 250°C. are suitable in this process, although as a general rule temperatures in the range of from about 150° to about 200°C. are adequate for commercially attractive rates of degradation of organic impurities without excessive hydrogen peroxide loss. At any given temperature the degree of

degradation of organic impurity will increase with the heating time, but longer heating times also increase the loss of hydrogen peroxide through undesirable reactions. It is therefore preferred to use heating times between about 30 sec. and about 1 hour. Most advantageously, times of about 1 to about 20 minutes are used when carrying out the treatment at the preferred temperatures of about 150° to 170°C. Best results are obtained by using the longer times at the lower temperatures and vice versa and maintaining the mixture substantially in the liquid state throughout the heat treatment.

As previously pointed out, hydrogen peroxide is corrosive, especially at elevated temperatures. On this account it is desirable to carry out the heat treatment in a corrosion resistant vessel. While glass or procelain surfaces are desirable because of their high resistance to corrosion, it is usually more advantageous in large commercial scale operations to use corrosion resistant metal vessels and/or heating tubes for the treatment. Tin, stainless steel, tantalum and zirconium surfaces are suitable when carefully cleaned and passivated in the way usual for apparatus in which hydrogen peroxide is to be used. Even with these surfaces some small amounts of catalytic metal ions may enter the peroxide under treatment through corrosion of the thermal reactor surfaces.

Because of this and as a safeguard against any catalytic metal ions that may inadvertently survive the ion exchange pretreatment, it is usually advisable to add an inhibitor of hydrogen peroxide decomposition. Sodium stannate ($Na_2SnO_3.3H_2O$) and sodium pyrophosphate ($Na_4P_2O_7.10H_2O$) are typical of the hydrogen peroxide stabilizers which can be used to reduce H_2O_2 loss in the thermal treatment step of this process. The amount of inhibitor should be kept to the minimum consistent with adequate hydrogen peroxide stability, when ion exchange is to be used for the following step of this process, namely, removal of the carboxylic acid which is formed in the thermal treatment. Quite small amounts of sodium stannate, for example about 2 to 50 mg. of $Na_2SnO_3.3H_2O$ per liter of peroxide solution, have been found to be sufficient. For instance, in heat treating in contact with stainless steel at 150°C., addition of 50 mg./l. of $Na_2SnO_3.3H_2O$ reduced the peroxide loss from about 5.5% to about 2.2% during degradation of 50% of the organic impurity.

On completion of the heat treatment, the carboxylic acid produced by the degradation of organic impurities is removed to obtain the desired purified hydrogen peroxide. The removal of the carboxylic acids is relatively easy by either distillation or ion exchange. Among suitable distillation methods are, for example, simple vacuum distillation, steam stripping, and extractive distillation with an inert solvent for hydrogen peroxide.

There are special advantages in using ion exchange resin for removal of the carboxylic acid formed in the preceding thermal degradation step of the process, since loss of hydrogen peroxide can be reduced by this method of operation. Any of the anion exchange resins described as useful in the preliminary treatment step of the process can be employed in this final acid removal operation. As previously pointed out, there are advantages in using strong base anion exchange resins of the quaternary ammonium base or tertiary sulfonium types, especially when these strong base resins are used in the form of their salts so as to avoid exposure of the peroxide to high pH at which hydrogen peroxide decomposes rapidly. The conditions and methods of application of the anion exchange resin and its regeneration after use can be varied.

It will usually be desirable to operate the anion exchange resin column differently in this case from that used to remove complexed metal anions prior to the heat treatment step where carboxylic acid removal was not necessary. For removal of carboxylic acids with anion exchange resin catalyst, one can advantageously use the method of Dunlop, Meeker and Pierotti in U.S. Patent 3,294,488 (59), since there will be no substantial amount of heavy metals present so carbon dioxide pressure will insure sufficient pH control through bicarbonate salt formation to prevent dangerous hot spot formation. Alternatively, one can use a monohydrogen phosphate salt of a strong base anion exchange resin to effect removal of the carboxylic acid, without displacing the phosphate ion from the resin but forming instead a mixed phosphate-carboyxlic acid salt of the resin.

Prior to the anion exchange resin treatment for removal of the carboxylic acids formed in the heat treatment step, it will be advantageous to employ another anion exchange resin treatment of the type previously described for removal of heavy metal ions if there has been substantial pickup of these ions in the heat treatment step. This will minimize peroxide decomposition due to hot spot and improve the life of the resin used for carboxylic acid removal.

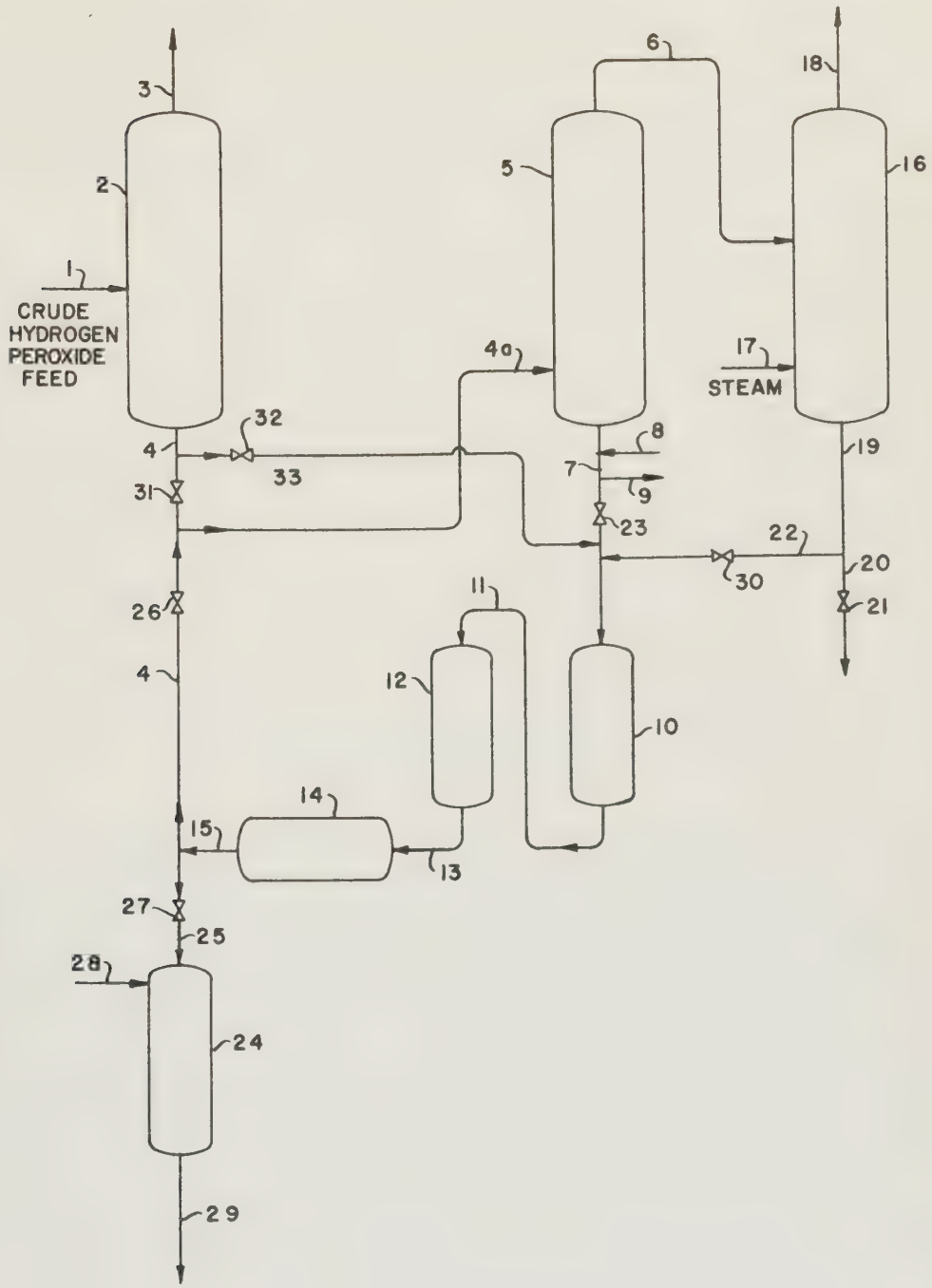
This process can be applied successfully to the purification of hydrogen peroxide containing organic impurities regardless of the source of the peroxide or impurities therein. However, peroxide which contains readily separable volatile organic impurities together with more difficultly separable organic impurities will usually be most economically purified by removing the volatile impurities which can be separated without danger of excessive peroxide loss prior to treatment by this method for removal of remaining less easily removed organic impurity. This is the preferred method of operation, for example, when purifying hydrogen peroxide produced by partial oxidation of an organic compound and containing both volatile and less volatile organic impurities.

Because of the technical importance of this application of the process, illustrations are given in Figure 4.4 of suitable methods of combining the process with other purification steps to obtain high purity hydrogen peroxide from such sources. The drawing is a flowsheet showing diagrammatically an assemblage of apparatus, not drawn to scale, suitable for carrying out certain of these modifications of the process but omitting, in the interest of simplicity and clarity, auxiliary equipment such as pumps, condensers, vacuum sources, etc., as well as valves, meters, gauges and the like, since their location in the system will be obvious to those skilled in the art.

In Figure 4.4, line 1 represents a supply line for the crude hydrogen peroxide to be purified. In the case of crude hydrogen peroxide produced by oxidation of a secondary alcohol, for example, isopropyl alcohol, this will be a stream of aqueous hydrogen peroxide containing approximately an equivalent amount of acetone, and unreacted isopropyl alcohol together with organic impurities some of which distill readily with the acetone and isopropyl alcohol, while a significant amount typically of the order of about 1 to about 2 parts per 100 parts of hydrogen peroxide will be higher boiling more difficultly removable organic impurities.

Line 1 feeds to column 2, in which the acetone and isopropyl alcohol content of the mixture is distilled off together with water carried overhead as the alcohol-water azeotrope. Organic impurities boiling in the same range will also be taken off by line 3. The column can be a conventional bubble-plate or grid-tray column or the like which can be operated at ordinary

FIGURE 4.4: COMBINED ION EXCHANGE AND HEAT TREATMENT PROCESS FOR PURIFICATION OF HYDROGEN PEROXIDE



Source: R.E. Meeker, A.K. Dunlop, D.B. Luten, Jr., U.S. Patent 3,074,782, January 22, 1963

or reduced pressures or at a superatmospheric pressure which is preferably not greater than about 25 psig. Since the object of the distillation in column 2 is simple removal of components more volatile than hydrogen peroxide, the temperatures and reflux ratios will be adjusted to that end and chemical changes will be minimized.

The bottom product from column 2 is conducted by lines 4 and 4a to a flashing column 5 operated at reduced pressure to take off hydrogen peroxide overhead by line 6 from higher boiling organic impurities taken off with a part of the hydrogen peroxide by bottom draw off line 7. Any conventional flashing still constructed of material inert to hydrogen peroxide decomposition can be used for this operation. The hydrogen peroxide is preferably flashed off rapidly without reflux, a pressure of the order of about 50 to about 500 mm. mercury being suitable.

In order to avoid explosive mixtures in the reboiler or elsewhere in the flasher, the bottoms product taken off by line 7 should not be too concentrated since its increased content of organic impurity makes it more hazardous at high peroxide concentrations. To further reduce the explosion hazard — here, particularly with regard to peroxide-resin mixtures — as well as to reduce attack upon the ion exchange resins, the bottom stream in line 7 is preferably diluted by water introduced by line 8 to bring the hydrogen peroxide concentration to below about 40% wt. A typical sample of such diluted flasher bottoms had the following gross analysis:

Hydrogen peroxide, percent wt.	35.5
Total carbon, percent wt.	1.1
Nonvolatile carbon, meq. per ml. [1]	0.44
Organic acid, meq. per ml.	0.10

[1] Not removed overhead by distillation, milliequivalent of carboxylic acid generated per milliliter of peroxide solution by analytical oxidation in alkaline solution at 60°C.

It is sometimes desirable to take off by line 9 a bleed stream of this peroxide in order to avoid excessive buildup of salts and the like in the system. The diluted flasher bottoms are fed to anion exchange column 10 which may advantageously be charged with a quaternary ammonium base resin in salt form. Good results have been obtained, for instance, with Dowex 1X8, 20 to 50 mesh, in nitrate form. Preferably the peroxide solution is cooled, by means not shown, to a temperature of about 35° C. or lower before being contacted with the resin since attack on the resin is reduced at low temperatures. Downflow, flooded bed operation is illustrated in the drawing, as channeling can be minimized by this method, but upflow or trickle downward flow can be used instead.

Only one anion exchange column is shown in the drawing, but in commercial practice it is usually desirable to employ at least two such columns in order that one can be regenerated or recharged with fresh resin, while the other is in its operating cycle so there need be no interruption of the flow of hydrogen peroxide through the system.

The columns will be provided with feed lines and drawoff connections, not shown, for use in regeneration and washing the resin in the conventional way. Tests of the column effluent for anionic heavy metal complex can be made periodically and the flow switched to the

regenerated column as soon as breakthrough of such complex reaches a predetermined value. Carboxylic acid will not be removed in this column which will selectively remove anionic heavy metal complexes from the peroxide. The effluent from anion exchange column 10 is passed by line 11 to cation exchange column 12 which is preferably charged with a strong acid exchange resin such as Dowex 50X8, 20 to 50 mesh, resin in hydrogen or sodium form. This column can be operated by the downflow, flooded bed system or any other conventional technique.

The effluent will be essentially free of heavy metal as shown by the following results obtained in deionizing a typical sample of flasher bottoms diluted to 39% H_2O_2:

	Feed to Deionization Columns	Deionized Product
Iron—mg. per liter	1.7	less than 0.01.
Copper—mg. per liter	0.03	less than 0.01.
Chromium—mg. per liter	0.66	less than 0.01.

The bulk of the metal ions were removed on the anion exchange resin, and without the use of this resin in combination with a cation exchange the hydrogen peroxide cannot be sufficiently freed of catalytic metal ions to eliminate the synergistic peroxide decomposition during the subsequent thermal treatment. The difference in rate of hydrogen peroxide decomposition achieved by this deionization is shown by the results of tests with the same hydrogen peroxide used for the foregoing metal analyses. Heating at 100°C. caused decomposition at the rate of 10.3% per hour in the crude flasher bottoms diluted to 39% H_2O_2, while after deionization the loss of hydrogen peroxide at 100°C. was only 0.25% per hour. The addition of fresh inhibitors to the deionized peroxide reduced the rate of decomposition still further.

The heat treatment step of the process is carried out in heater 14 to which the hydrogen peroxide is fed directly by line 13 from cation exchange unit 12. Heater 14 may take any form suitable for heating the peroxide in liquid phase and maintaining it at the required temperature for sufficient time to effect the desired degradation of organic impurity. One design, which has been found satisfactory for this treatment, comprises a preheater, advantageously heated by high pressure steam, e.g., of about 250 psig.

Directly connected to the preheater is a pipeline reactor constructed of several passes of pipe to provide a residence time of about 1/2 to 30 minutes, when using a temperature of about 200° to about 130°C. for instance. The effluent is cooled by means not shown and any gas present is preferably separated in a de-entrainment unit, also not shown, after which the treated hydrogen peroxide is passed by line 15 to lines 4 and 4a feeding to flashing unit 5. In flasher 5, the volatile carboxylic acid formed in the heat treatment in unit 14 will be taken off overhead by line 6 along with hydrogen peroxide and water coming in part from column 2 and in part from heater 14.

The overhead product from flasher 5 taken off by line 6 is treated to separate the volatile organic impurities, chiefly carboxylic acid, from the hydrogen peroxide. This can be accomplished in a number of different ways. Anion exchange resin treatment is one suitable

method but, as previously pointed out, should be carried out differently from the anion exchange used in column 10, where the purpose was removal of catalytic metal ions present in anionic form as a result of complex formation with the peroxide stabilizer present and where carboxylic acid removal was not necessary.

For anion exchange resin treatment of flasher 5 overhead, one can advantageously use one of the previously mentioned methods employing salts of strong base exchange resins. Steam stripping is an alternative which is advantageous and is shown as carried out in column 16, with steam admitted by line 17. Carboxylic acid together with small amounts of other volatile organic impurities are taken off via line 18, while purified hydrogen peroxide is recovered by line 19 and line 20 containing valve 21. The degree of purification of this hydrogen peroxide product will depend upon the time of treatment used in heater 14. The loss of peroxide in the process increases with the conversion of organic impurity. Above about 70 to 80% conversion, the rate of degradation of organic impurity falls off and the loss of hydrogen peroxide per pound of organic impurity converted increases, so it is generally more advantageous not to carry the conversion beyond these limits. By such operation this method can be carried out to produce hydrogen peroxide having a carbon content of less than 100 parts per million, usually between about 20 and about 50 parts per million, with the loss of not more than 4%, and usually about 1 to 2.5%, of the hydrogen peroxide.

Typical results obtainable by this method of operation in which the feed to the system was the crude hydrogen peroxide product of oxidation of isopropanol, are shown in the following table for various temperatures and times of heat treatment of the flasher bottoms which were deionized with Dowex 1X8, nitrate form, and Dowex 50X8, hydrogen form, ion exchange resins from Dow Chemical Co., and inhibited with 125 mg. per liter of sodium pyrophosphate. The feed to the heater in each case had a H_2O_2 concentration of 31.84% and contained 0.381 meq. per milliliter of nonvolatile organic impurity and 0.088 meq. per milliliter of acids.

Heating Temperature (° C.)	Time of Heating (min.)	Non-Volatile Organic Impurity Degraded (mole percent)	Loss of H_2O_2 (percent of total)
132	10	28.7	1.8
	30	41.4	4.5
	53	52.7	4.9
150	6.5	44.6	1.7
	10	48.6	2.9
	15	55.2	5.5
	23	62.0	6.6
	32	69.3	7.6
167	6	73.2	9.4

Another Shell Oil exchange resin process for H_2O_2 purification has been described by D.B. Luten, Jr. and R.E. Meeker, in U.S. Patent 3,156,531 (58); it is especially designed to remove dissolved acids.

CONTACTING WITH ANION EXCHANGE RESIN IN BICARBONATE SALT FORM

Shell Oil Co.; Dunlop, A.K., Meeker, R.E., and Pierotti, G.J. (59): Aqueous hydrogen peroxide containing acid impurity is purified by contact with anion exchange resin in bicarbonate salt form. This method of acid removal has the advantage that very complete removal of acid can be achieved without danger of loss of hydrogen peroxide through decomposition.

In carrying out the process, it is desirable to use an anion exchange resin which is resistant to attack by the hydrogen peroxide solution under the conditions used for the purification. It is necessary to employ a strong base resin of the quaternary ammonium salt type as distinguished from the weak base resins (primary, secondary and tertiary amine type resins) normally used for removing unionized acids from aqueous solutions. Also, carboxylic acid removal is more complete with strong base resin.

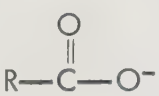
Examples of strong base resin which are advantageously used in the process are the products of amination with trimethyl amine; for instance, a chloromethylated styrene-divinyl benzene copolymer as described in U.S. Patent 2,591,573 and sold by Rohm and Haas under the trade names Amberlite IRA-400 and Amberlite IRA-401; anion exchange resins made by the process of U.S. Patent 2,388,235 and the resins sold by Dow Chemical Company under the trade names Dowex 1, Dowex 2, and Dowex 21K or by National Aluminate Corporation under the trade name Nalcit SBR. Duolite A42, A101 and A102, made by Chemical Process Company, Redwood City, California, are other anion exchange resins suitable for use in the process.

These strong base resins cannot be used in the free base form, because the high pH would lead to undesirable hydrogen peroxide decomposition during the purification. This is avoided by using the anion exchange resin in bicarbonate salt form.

The bicarbonate salts of the anion exchange resins have outstanding advantages over any other salt form. Not only do these salts make it easy to maintain the pH of the hydrogen peroxide in the desired range below about 6.5, which is desirable for maximum stability, but also these salts avoid introduction of other impurities into the peroxide solution. By use of this salt, acid impurities in the hydrogen peroxide are exchanged for bicarbonate which is eliminated from the solution as carbon dioxide using the hydrion of the acid being removed. The net reaction is conversion of the bicarbonate salt regenerant to carbon dioxide which is volatilized and salts of the acid impurities, which salts are led off in the regeneration of the anion exchange resin. The reaction of the resin salt can be written: -

$$\text{Resin-HCO}_3 + \text{H-X} \rightleftharpoons \text{Resin-X} + \text{H}_2\text{O} + \text{CO}_2\ (\text{gas})$$

where resin represents the anion exchange resin and X is the anion of the acid being removed, e.g., $H_2PO_4^-$ in the case of phosphoric acid or



in the case of carboxylic acids; here R is hydrogen or an organic radical, for example, a lower alkyl radical. Thus, the exchange is driven to completion through removal of the product HCO_3^- ion via release of gaseous carbon dioxide. The only products put into the hydrogen peroxide solution are water and a very small amount of CO_2. This is in contrast to other salt forms of the resins, which introduce an equivalent of acid for each equivalent removed.

This especially advantageous modification of the process, control of pH in the range of about 3 to about 8, which is desirable for limiting hydrogen peroxide decomposition, is easily accomplished by controlling the partial pressure of carbon dioxide in the system. Operation at a pH of from 4 to 6.5 is particularly advantageous. The pH's here referred to are those measured in the exit stream and refer to the true pH of the peroxide solution which requires application of a correction to glass electrode readings in hydrogen peroxide solutions, as pointed out by J.R. Kolczynski et al in the Journal of the American Chemical Society, vol. 79, page 531 (1957).

Only a small partial pressure of carbon dioxide is necessary for this pH control, the CO_2 generated in the exchange reaction being generally adequate when carrying out the purification at the preferred temperatures of about 25°C. or below. It is usually desirable, however, to carry out the purification with a small amount of added carbon dioxide even at these low temperatures of operation, in order to provide against undesirable rise in pH with accompanying loss of hydrogen peroxide should there be an interruption in the flow of solution through the resin or nonuniform distribution of solution on the resin, so that CO_2 generation by exchange is inadequate to maintain the desired buffering action.

The partial pressure of carbon dioxide which will be most desirable will depend upon the temperature, composition of the hydrogen peroxide feed, particularly with respect to the salt content, and on the pH which it has been decided to maintain. The lower the pH desired or the higher the temperature, or the higher the salt content, the higher will be the carbon dioxide partial pressure required under otherwise similar conditions. For instance, with one salt-containing feed containing 0.08 N organic acids, the CO_2 generated by the exchange at 40°C. maintained the pH at 6.4, while additional CO_2, of partial pressure about 0.25 atmosphere, lowered the pH to 5.5.

As the temperature is increased the life of the anion exchange resin decreases, so it is desirable to carry out the purification at temperatures below 80°C., and more preferably between about 10° and about 25°C.

The time of contact of the hydrogen peroxide solution with anion exchange resin bicarbonate salt can vary widely. Excessively long times of contact which lead to undesirably short resin life per volume of hydrogen peroxide treated (due to attack on the resin by the peroxide) are of course to be avoided, especially since relatively short times of contact are sufficient in order to secure adequate removal of acid impurities. Thus, times of the order of about 10 sec. to about 1 hour are suitable, and more preferably times of about 1/2 to about 15 minutes are used.

The hydrogen peroxide solution to be purified can be contacted with the anion exchange resin bicarbonate salt in different ways. One simple method is to stir a slurry of the resin

salt and hydrogen peroxide solution in which about 10 to about 50 parts by weight of resin salt are used per 100 parts of solution for a time as indicated above, subsequently separating the solution from the resin by decantation, filtration or centrifugation. During contacting, the pH should be maintained in the proper range by application of an appropriate partial pressure of CO_2, as by bubbling the gas through the slurry.

More advantageously, the anion exchange resin in bead or other particulate form is used as a bed through which the hydrogen peroxide solution to be purified is passed. The solution can be contacted with the resin bed by upward or downward flow. The carbon dioxide and any oxygen from trace decomposition of hydrogen peroxide released sometimes tends to cause channeling and, consequently, poor operation. This can be minimized by operating under pressure sufficient to keep the carbon dioxide dissolved.

The problem can be completely overcome by dispersing the solution over the bed as a downwardly flowing stream, using a gas for dispersion of the solution as a relatively thin film over the resin surface. This gas should be inert under the conditions employed. The required amount of carbon dioxide for maintaining the desired pH can be added with the dispersing gas which may be air, nitrogen or the like. Alternatively, flooded bed operation using a down flow liquid rate sufficient to sweep gas down through the bed, e.g., 5 to 7 feet or more per hour, can be used with good results. Similar methods of operation without addition of carbon dioxide can also be employed, by using high space velocities and uninterrupted operation; but addition of carbon dioxide is more advantageous.

The removal of acids in this way can be effected essentially quantitatively, and a rather sharp breakthrough of acids occurs due to use of the anion exchange resin in bicarbonate form. A high degree of utilization of resin capacity is also realized. Upon or just before such breakthrough, the resin can be regenerated and used again in the process through many cycles; so the cost of resin in the process is very low.

The anion exchange resin can be regenerated in various ways. For example, the regeneration can be carried out with a solution of a salt of carbonic acid so as to make the bicarbonate salt directly. Sodium bicarbonate, for example, is a suitable salt for regeneration in this way. Alternatively, the resin can be treated with base in the usual way to convert it to the free hydroxide form which can then be washed with a solution of carbonic acid or with water and CO_2 gas in excess of its water-solubility, to make the desired bicarbonate salt. However, as a general rule it is preferred to carry out regeneration of the exhausted resin with a sodium carbonate solution, followed by washing with CO_2 and water to convert the carbonate salt to the bicarbonate resin salt, since more complete regeneration can usually be obtained in this way.

The process can be carried out with impure hydrogen peroxide solutions of any concentration. With hydrogen peroxide solutions of 90% weight concentration or higher, there is a definite detonation hazard which should be guarded against. With an initial peroxide concentration of 49% weight or more, detonations are still possible if the resin has become so thoroughly degraded by excessive service that it is capable of forming a homogeneous solution with the peroxide solution being treated. Therefore, solutions of not more than about 50% weight hydrogen peroxide are preferably used in the process.

The process is especially advantageous for the purification of hydrogen peroxide containing a minor amount, i.e., less than about 0.5 N, preferably between about 0.01 N and about 0.1 N, of acid impurities. Most desirably, the hydrogen peroxide solution to be purified is substantially free of ions which catalyze hydrogen peroxide decomposition, particularly ions of iron or other heavy metals. Removal of such ions markedly increases the effective life of the anion exchange resin employed in the process. U.S. Patent 2,676,923 describes one method of removing metal ions from hydrogen peroxide solutions, by means of cation exchange resins, which can be employed for this purpose; but other suitable methods can also be used. The process is further illustrated by the following example.

The results obtained with two 100 milliliter resin beds (2.5 x 21 cm.) of Dowex 1 x 7.5, a trimethyl benzyl ammonium poly(styrene-divinylbenzene) anion exchanger (20 to 50 mesh), demonstrate the efficiency of the method and illustrate its flexibility. One resin bed, bed A, was regenerated with 700 milliliters of a 5% by weight sodium bicarbonate solution; and the other bed, with about 800 milliliters of 5% by weight sodium carbonate solution. Through bed A, an impure aqueous 16% by weight hydrogen peroxide solution, about 0.065 N in carboxylic acids, was passed at about 20°C. at the rate of 3 bed volumes per hour. The liquid was distributed over the beads in a film by a flow of air plus 5% CO_2, at the rate of 850 bed volumes perhhour.

Through the other bed, an impure aqueous 21% by weight hydrogen peroxide solution of similar acid content was passed at 40°C. at the rate of 7.5 bed volumes per hour. Liquid distribution was obtained with an inert gas, air, flow of 600 bed volumes per hour. Bed A removed 99% of the acid in the feed until some 83% of the ultimate capacity of the bed was saturated, at which time the acid broke through into the column effluent and the pH fell from 5.8 down toward that of the feed. In the other column, acid removal was 98% and bed utilization to breakthrough was 82%.

Two further recent purification processes utilizing ion exchange resins are disclosed in U.S. Patent 3,297,404 (60), assigned to Du Pont; and U.S. Patent 3,305,314 (61), to Pittsburgh Plate Glass Co.

TWO-STAGE SOLVENT EXTRACTION USING AN ORGANIC SOLVENT MIXTURE OF HYDROCARBON AND POLAR CONSTITUENTS

Laporte Chemicals Ltd.; Williams, S.D. (62): A process is provided for the purification of hydrogen peroxide produced in a cyclic process involving the alternate reduction and oxidation of an organic intermediate. The hydrogen peroxide is treated with at least one organic solvent mixture which contains at least one hydrocarbon solvent constituent and at least one polar solvent constituent, and is subsequently separated from the solvent mixture. Desirably, in the solvent mixture the ratio of the hydrocarbon content to the polar solvent content is never less than 0.7:1 and preferably at least 1:1.

Advantageously, the crude hydrogen peroxide is subjected to two extraction steps, the first being with a solvent mixture in which this ratio is about 1:1, for example in the range of 0.9:1 to 1.2:1, the second with a solvent mixture in which the ratio is at least 2:1, desirably about 3:1 to 4:1. The first treatment has the general effect of removing hydrophilic

impurity, but this is accompanied by a certain amount of the polar solvent constituent of the solvent mixture being dissolved in the hydrogen peroxide. The second treatment has the dual effect of removing from the hydrogen peroxide both nonhydrophilic impurity and at least part of the dissolved solvent.

From the point of view of loss of hydrogen peroxide into the extraction solvent, it is found that with solvent mixtures in accordance with the process the loss is only slightly less, for example, about one-third, than that incurred by employing a polar solvent alone.

The example given subsequently shows the advantageous results obtained by the process as compared with extraction with single solvents. Suitable solvents for use as the hydrocarbon constituent are: xylene, or mixtures of aromatic hydrocarbons sold under the trade names Aromasol (BP > 145°C.), or Shellsol A (BP >185°C.); higher alkanes, for example C_7 to C_{10} alkanes such as heptane and decane; and cyclohexane. Suitable solvents for use as the polar constituent are methylcyclohexyl acetate, diisobutyl carbinol, and decanol.

In a preferred embodiment of this process, the crude hydrogen peroxide is given a two-step treatment of the type referred to above. The solvent mixtures are two fractions derived from a cyclic hydrogen peroxide manufacturing process employing an organic solvent mixture of hydrocarbon and polar constituents. After being used on the crude hydrogen peroxide, the solvent mixtures are returned to the cyclic process. The impurities which the solvent mixtures contain will thus be incorporated into the cycle. However, it is surprisingly found that the impurities are revertible by the regeneration step which is normally incorporated into the cycle, and this of course tends to reduce or eliminate buildup of impurity.

The solvent fractions employed can be obtained from any suitable stage of the cyclic process for producing hydrogen peroxide. Thus, for example, they can be taken from the gas effluent line from the oxidizer. Two quite distinct fractions can be obtained. The first, formed by condensation in the effluent line, normally has a ratio of hydrocarbon:polar constituents of about 1.5:1, although this ratio can obviously be varied if desired by altering the condensation conditions. The second is obtained from the carbon absorption beds in the effluent line, and normally has a ratio about 4:1, although again this may be varied as desired. As a further example, the fractions can be derived directly from the solvent of the cycling solution. One suitable way of deriving these fractions is to flash them off from the feed to or effluent from the regeneration step, which is normally incorporated into a cyclic process for producing hydrogen peroxide.

The relative volumes of solvent mixture used can vary considerably. Thus the ratio solvent mixture:crude hydrogen peroxide may be as much as 1:1, or as little as 1:100, even 1:200. Whenever possible, it is desirable to conduct the impurity extraction as a countercurrent process. It is convenient to work at temperatures of from 20° to 25°C., although higher temperatures may be employed if desired.

Advantages arising from using this preferred embodiment may be briefly stated as follows:

(1) The solvent mixture used for extraction is derived from the cyclic process and is returned to it without upsetting the solvent balance within the cycle.

(2) The impurity extracted into the solvent is reverted to useful hydrogen peroxide-producing material, by a well-known regeneration process.

(3) While a purely hydrocarbon solvent might possibly give an equally efficient extraction, use of this one solvent alone might upset solvent balance in the cycle if returned to it; or if not returned, might require expensive recovery treatment.

(4) Advantages over polar solvent alone are that no further treatment of the hydrogen peroxide is necessary to remove solvent dissolved in hydrogen peroxide, and less hydrogen peroxide itself is extracted into the solvent and either recycled — if the polar solvent is fed back to the cycle — or lost, of another recovery system is employed.

The following example compares the results obtained by using a solvent mixture in accordance with the process, and results obtained using a single solvent. The impurity figures relate to nonvolatile impurity, that is to say, impurity which remains even after concentration of the crude hydrogen peroxide to 40% of its original volume. In each case, the solvent:crude hydrogen peroxide ratio was 1:1. The hydrogen peroxide was obtained from a cyclic process employing 2-ethyl anthraquinone in a hydrocarbon/ester solvent mixture. The impurity figures given are measured as carbon.

	Mg./l.
(a) Initial impurity content	580
After treatment with xylene	450

There was negligible extraction of hydrogen peroxide into the xylene.

	Mg./l.
(b) Initial impurity content	580
After treatment with methyl cyclohexyl acetate	390

About 2% of the hydrogen peroxide was extracted into the methyl cyclohexyl acetate.

	Mg./l.
(c) Initial impurity content	580
After treatment with 1:1 mixture of xylene and methyl cyclohexyl acetate	370

Less than 0.5% of the hydrogen peroxide was extracted into the solvent mixture.

PRECIPITATION OF IMPURITIES BY MEANS OF FLOCCULATING AGENT AND pH ADJUSTMENT

FMC Corp.; Flach, D.O., and Siwinski, G.W. (63): It has been found that deleterious impurities can be removed readily from an aqueous acidic hydrogen peroxide solution having a pH of less than about 5 by a process which involves adding to the hydrogen peroxide solution, sufficient hydrogen peroxide-compatible alkali to adjust the pH of the solution to from about 5.6 to 7.5, thereby causing impurities to convert to insoluble solids, and separating

these solids from the solution. Where the hydrogen peroxide is to be distilled and/or stored for a substantial time, the pH of the hydrogen peroxide is then preferably adjusted to about 1.2 to 3.5 with a hydrogen peroxide-compatible acid to provide a stable environment for this hydrogen peroxide.

In the preferred embodiment of this process, an aqueous acidic solution of hydrogen peroxide is first treated by addition of a metal salt which is soluble in aqueous hydrogen peroxide at a pH of less than about 5 and which at a pH of about 5.6 to 7.5 converts to an insoluble condition. Typical useful salts are aluminum sulfate and the like. Following this, the pH of the resulting aqueous solution is raised to about 5.6 to 7.5 with a hydrogen peroxide-compatible alkali, whereupon the metal salt is converted to an insoluble condition (in the case of aluminum sulfate to aluminum hydroxide, a flocculating agent) and the impurities in the hydrogen peroxide are caused to precipitate. This coprecipitation of the flocculating agent from the metal salt and the impurities in the hydrogen peroxide results in adsorption of the impurities on the flocculating agent, thereby facilitating their physical removal from the solution. The resulting purified aqueous hydrogen peroxide solution may then be treated by addition of an acid to change it to a pH on the order of 1.2 to 3.5, as described above, where it is desirable to do so.

It is surprising that this process operates to improve stability of aqueous hydrogen peroxide solutions by removal of impurities therefrom, without itself effecting substantial decomposition of the sensitive active oxygen compound. Hydrogen peroxide is known to be especially susceptible to decomposition at pH's above about 5 to 6, and this process operates by raising the pH of the aqueous hydrogen peroxide solution to about 5.6 or higher, while the impurities are in a particularly active state.

The hydrogen peroxide treated by the process has a pH of less than about 5, usually on the order of 0.5 to 5, and when derived from inorganic processes usually contains catalytic inorganic impurities in the amount of 0.2 to 10 parts per million. These catalytic impurities comprise soluble salts of iron, chromium, copper, manganese and other materials, all of which have a deleterious effect on the hydrogen peroxide, particularly at elevated temperatures and at an elevated pH.

Hydrogen peroxide produced by organic processes contains substantial amounts of these metallic impurities, and also organic impurities carried over from the working solutions employed to produce the hydrogen peroxide. These impurities are produced by decomposition of the hydrogen peroxide-producing working solution, and are evidenced by discoloration of the hydrogen peroxide when it is stored for on the order of 24 to 72 hours at ambient temperatures, or when it is heated to about 70° C. for 3 to 4 hours.

Both described kinds of impurities have a deleterious effect on the stability of the hydrogen peroxide solution on storage, and it is therefore desirable to remove them from the solution. This process reduces the inorganic contaminants to a concentration of on the order of 0.06 to 0.10 ppm when not employing a flocculating agent, and to as low as about 0.04 to 0.08 ppm when the flocculating agent, preferably aluminum sulfate, is employed. With respect to the organic impurities, it has been found that the color value of an aged hydrogen peroxide can be cut in half or reduced even further by this process.

The hydrogen peroxide treated by this process normally has a concentration of about 15 to 35%. However, the process can be used to treat aqueous acidic hydrogen peroxide at any concentration.

The alkali employed to treat the hydrogen peroxide is one which is compatible with hydrogen peroxide, for example ammonium hydroxide, sodium hydroxide, potassium hydroxide or anhydrous ammonia. Other hydrogen peroxide-compatible alkaline agents may be employed and such alkalis are well-known. They are added in an amount to raise the pH of the solution to about 5.6 to 7.5. If a pH below 5.6 is employed, incomplete precipitation of impurities and also of the flocculating agent, where it is used, occurs. If a pH above 7.5 is employed, an unstable condition is created.

In the preferred embodiment of this process, an aluminum or other flocculant-producing salt is added to the aqueous hydrogen peroxide solution prior to addition of the alkali. These salts preferably are aluminum salts such as aluminum sulfate, aluminum nitrate, aluminum chloride, aluminum potassium sulfate and aluminum ammonium sulfate, although magnesium salts such as the sulfate may be employed in their place. They are employed in amounts of about 0.005 to 0.080 gram per liter expressed as metal ion; if less than the lower amount is employed, they do not provide effective assistance in removal of precipitated impurities, while addition of more than the upper indicated amount confers no added benefit.

Acid preferably is used to adjust the final pH of the aqueous hydrogen peroxide solution, following treatment with alkali and removal of precipitated impurities, to about 1.2 to 3.5. This treatment is carried out when use of the hydrogen peroxide calls for an acid system, or where the hydrogen peroxide solution is to be shipped or stored for a substantial time; in the latter case, the solution is acidified to create a favorable environment for stability of the hydrogen peroxide. In connection with stability, the usual hydrogen peroxide stabilizing agents, for example, dipicolinic acid, tin salts, sequestering agents, and the like may be added to the purified hydrogen peroxide solution to provide maximum stability on storage or in use.

Useful acids for adjusting the pH of the purified hydrogen peroxide solution include phosphoric acid and sulfuric acid. The phosphoric acid is particularly suitable since it has a stabilizing effect on active oxygen compounds in addition to its pH-adjusting effect. It is apparent that acids such as hydrochloric acid which act to decompose hydrogen peroxide are not to be employed.

The process is preferably carried out at ambient temperatures, for example at about 15° to 25°C.; at elevated temperatures hydrogen peroxide stability decreases, particularly in the presence of impurities, so that it is not desirable to operate above about 25°C., and there is no need to refrigerate the system to operate below about 15°C. However, if desired, the process can be carried out at any temperature between the boiling and freezing points of the solutions, provided the normal decomposition of the hydrogen peroxide at elevated temperatures can be tolerated.

Simple mixing procedures can be employed to carry out the mixing of ingredients; there is no need to employ special mixing equipment. Removal of precipitated ingredients can be effected by ordinary physical separation methods such as filtration, centrifugation and the

like. The following is an example of the purification process.

An aqueous hydrogen peroxide solution having a true pH of 1.8 and a concentration of 50% of hydrogen peroxide was obtained by electrolysis of ammonium bisulfate to ammonium persulfate and hydrolysis of the latter, followed by distillation of the hydrogen peroxide which was received at a concentration of 27 1/2%. This hydrogen peroxide solution contained catalytic inorganic impurities to the extent of about 0.53 ppm, including about 0.33 ppm of iron ions, 0.05 ppm of copper ions and about 0.15 ppm of chromium ions.

About 7 ml. of 28% aqueous ammonium hydroxide solution was added to one liter of this aqueous hydrogen peroxide solution to raise its pH to 5.6. The treatment was carried out at 35°C. for 15 minutes with stirring. A precipitate formed upon addition of the alkali and was filtered from the solution. The pH of the solution was then dropped to 2.1 with phosphoric acid. The iron content of the solution was reduced from its initial level of 0.33 to 0.04 ppm, copper from 0.05 to 0.02 ppm, and chromium from 0.15 to a final 0.03 ppm. The stability of the hydrogen peroxide was improved from 63% loss of hydrogen peroxide at 100°C. in 6 hours to 14% loss at 100°C. in 6 hours.

CONCENTRATION

As we have seen in previous chapters, hydrogen peroxide is usually produced in the form of a relatively dilute and impure solution which needs further purification and concentration. This chapter is primarily concerned with the latter aspect, although certain concentration processes also effect a certain amount of purification.

The crude hydrogen peroxide solution commonly contains from 10 to 30% of H_2O_2, and is usually contaminated with carbonaceous impurities. Unless special precautions are taken, purification and/or concentration by vacuum distillation is hazardous. The presence of carbonaceous substances in large amounts renders the hydrogen peroxide explosive at certain concentrations, say 70%. On the following pages, special fractionation arrangements are described, which all claim to effect concentration and/or purification of H_2O_2 safely, with little or no danger of explosion.

COLUMBIA-SOUTHERN (PPG)

Straub, W.S., and Sindlinger, C.J. (46): A method has been provided whereby hydrogen peroxide, containing carbonaceous impurities, may be vaporized safely and with substantially little danger of explosion. In the practice of this process, an aqueous hydrogen peroxide solution containing carbonaceous impurities is heated in a vaporizer to partially vaporize the solution and thereby form a mixture of vapor and unvaporized liquid residue. Normally less than 20%, by volume of the solution, is vaporized in a single pass of the solution through the vaporizer.

The resulting mixture of vapors and unvaporized liquid hydrogen peroxide solution is carried upward in the vaporizer by the rising vapors and is discharged from the upper portion of the vaporizer, while at the same time a body of unvaporized hydrogen peroxide solution is maintained in the lower portion of the vaporizer. The mixture thus discharged is delivered to a separator where the vapor is separated from unvaporized hydrogen peroxide and the latter is then delivered to the body of hydrogen peroxide solution in the vaporizer, usually at a point below that at which the vapors are formed in the vaporizer.

Thus, a cycle is established in which hydrogen peroxide solution circulates upwardly through the vaporizer into the separator and back into the bottom of the vaporizer. As a consequence, a relatively concentrated hydrogen peroxide solution containing in the range of about 55 to 70% by weight of hydrogen peroxide is established in the circulating system. Hydrogen

peroxide feed solution to be vaporized is supplied to the body of liquid in the bottom of the vaporizer continuously; in order to avoid excessive concentration of carbon in the circulating body of liquid, a quantity of liquid hydrogen peroxide is purged from the body of liquid returning to the vaporizer either continuously or from time to time.

In the operation of the process as indicated above, there is serious danger that the hydrogen peroxide solution may rise in concentration above that at which an explosive hazard is created. Where the carbon concentration is high, any concentration above 70% H_2O_2 by weight is hazardous. If the concentration of carbon is low, on the other hand, higher H_2O_2 concentrations can be safely reached. Undue concentration of the solution can occur inadvertantly for a number of reasons.

In the first place, the rate of heat input into the vaporizer may be so fast as to cause vaporization of the solution at a rate faster than the feed is supplied. Secondly, stoppage can occur in the hydrogen peroxide feed lines coming from the hydrogen peroxide tanks, of which the operator may be unaware. In either case, the hydrogen peroxide continues to circulate in the vaporizer-separator loop, becoming more and more concentrated as vapor is removed.

In this process, the likelihood of this hazard taking place is eliminated or at least substantially minimized by providing a reservoir or pool of dilute hydrogen peroxide in direct and unobstructed communication with the body of solution in the bottom of the vaporizer at a point below that at which the vapors are formed in the vaporizer. Thus, the hydrogen peroxide feed is delivered from the pool or reservoir at a point well below that at which the vapors are heated; furthermore, the level of the pool in the reservoir is maintained substantially equal in height to that of the body of liquid in the vaporizer while the weight of liquid in the pool or reservoir is maintained at least five times the weight of liquid in the vaporizer (which, of course, includes any portion of the body of liquid extending into the return line coming from the separator).

As a consequence, whenever feed of hydrogen peroxide to the reservoir should be discontinued, the level of the liquid in the reservoir gradually falls but is always present in amount sufficient to dilute the body of hydrogen peroxide solution established in the vaporizer below 70% by weight. This dilution is inevitable and inherent because of the greater volume of solution in the reservoir than in the vaporizer.

Consequently, so long as the concentration of the hydrogen peroxide supplied to the reservoir is less than that produced after vaporization of a portion of the hydrogen peroxide and water therefrom, the dilution will inevitably occur by the hydrogen peroxide coming from the reservoir, thereby maintaining the hydrogen peroxide solution below the explosive concentration, even though vaporization continues to occur and the level of liquids in the reservoir and the vaporizer continues to fall.

As vaporization is continued in such a system, a stage is finally reached when the amount of vapors formed in the vaporizer will not be great enough in volume to carry hydrogen peroxide liquid solution into the separator. Even in that case, dilute hydrogen peroxide solution continues to flow from the reservoir, thus preventing concentrations of the solution in the vaporizer beyond the safe limit. However, it often occurs that the level of the hydrogen peroxide in the vaporizer rises and falls, creating a pulsation in the bottom of the vaporizer

which communicates itself into the reservoir, thereby causing an appreciable mixing of the hydrogen peroxide in the reservoir with the hydrogen peroxide in the vaporizer. This mixing also promotes dilution of the hydrogen peroxide in the vaporizer system below the explosive concentration, although the process will function effectively even without such back-mixing.

As shown in Figure 5.1, there is illustrated a vaporizer tube 10 enclosed in steam jackets 12 which terminate a substantial distance above the lower end of the vaporizer tube. The vaporizer tube is provided with an outlet 14 in its upper end, which discharges into a separator chamber 16 which may conveniently be a large cylindrical chamber in which the vapors may separate from liquids. The separator chambers 16 may also be provided with scrubbing trays or packing which is adapted to facilitate separation of liquids from gases. The separator discharges into conventional equipment used for the recovery and/or rectification of hydrogen peroxide vapor.

Separator 16 is also provided at the lower portion with a discharge line 18 which delivers separated hydrogen peroxide liquid solution to a header 20, which communicates with the bottom of vaporizer tube 10 and is disposed a distance appreciably below the point at which heat is applied to tube 10.

Also connected to the header is an open, unobstructed line 30 for supplying hydrogen peroxide feed solution to the header and, further, there is provided a suitable purge line (not shown) for removing hydrogen peroxide solution periodically or continuously from the header.

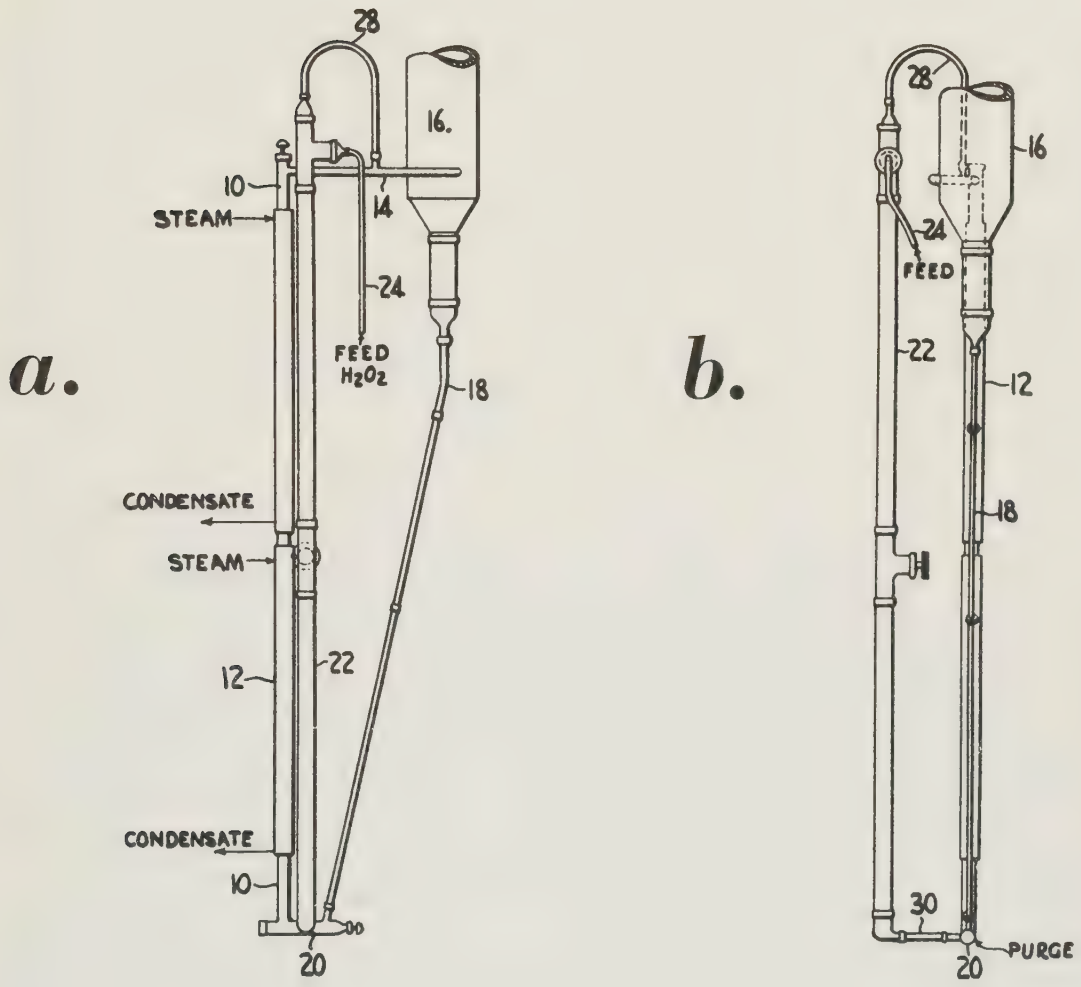
Line 30 is connected to a reservoir 22. The cross-sectional area of reservoir 22 is substantially in excess of that of tube 10, normally being large enough to hold at least five, and preferably at least nine, times the weight of hydrogen peroxide solution that can be held (at any given level common to the reservoir and the vaporizer) in the vaporizer (including tube 10 and tube 18).

The reservoir is disposed at substantially the same level as that of the vaporizer, so that a pool of hydrogen peroxide established in the reservoir takes substantially the same level as the level of liquid in the vaporizer. In order to ensure that this occurs, a line 28 is provided to communicate with the upper portion of the vaporizer and also with the vapor space in the separator, for example, through line 14, so that the pressure in the upper portion of the reservoir in the vapor space above the level of the pool of hydrogen peroxide is maintained equal or substantially equal to that in the vapor spaces in the vaporizer and the separator.

Hydrogen peroxide solution is supplied from a feed tank (not shown) to the reservoir through line 24, and a pool of liquid is established therein at a suitable depth, for example, a depth equal to about half the height of the vaporizer. Because line 30 is substantially unobstructed and is free from valves, hydrogen peroxide flows from the reservoir through line 30 into the vaporizer, thereby establishing a level of liquid in the vaporizer (particularly tube 18) substantially equal in height to that in the reservoir. Heat is then applied by passage of steam through the jackets 12, and hydrogen peroxide is caused to vaporize.

As a consequence of this vaporization, a mixture of vapor and hydrogen peroxide solution

FIGURE 5.1: APPARATUS FOR CARRYING OUT THE COLUMBIA-SOUTHERN (PPG) CONCENTRATION PROCESS



Front elevation

Side elevation

Source: W.S. Straub, C.J. Sindlinger, U.S. Patent 2,960,448, November 15, 1960

rises through the tube 10 and is discharged through line 14 into the separator 16, carrying unvaporized liquid therewith. The rate of application of heat is controlled so as to prevent evaporation of more than about 50% by weight of the solution. The resulting mixture thus contains at least half of the original mixture in the form of an unvaporized liquid.

The unvaporized liquid is separated in separator 16 and is returned through line 18 to the header 20 from where it is then returned to the vaporizer. Continuously or from time to time, hydrogen peroxide purge is withdrawn from the header 20. Continued heating produces a more or less continuously circulating stream of liquid which flows upwardly through the vaporizer into the separator, returning downwardly to the vaporizer. The concentration of this aqueous solution normally ranges between about 55 to 70% by weight of hydrogen peroxide.

The concentration of the hydrogen peroxide feed should be less than 60% by weight, preferably in the range of 5 to 35% by weight of hydrogen peroxide. The amount of carbonaceous impurities which are present in this material will depend upon its method of manufacture, but frequently the total carbon in the hydrogen peroxide will range from 0.2 to 5.0 grams per liter of hydrogen peroxide solution. As a consequence of the removal of vapors which contain less carbonaceous material than does the residual liquid, the concentrated hydrogen peroxide solution circulated through the vaporizer frequently will contain 2 to 25 grams per liter of hydrogen peroxide.

If any stoppage in the feed of hydrogen peroxide to the reservoir through line 24 should occur without knowledge of the operator, vaporization of the hydrogen peroxide will, of course, continue. This simply causes a fall in the level of the hydrogen peroxide in the vaporizer and a consequent fall of the level of hydrogen peroxide in the reservoir 22. However, since the cross-sectional area of the reservoir is large enough to maintain at all times a much larger volume of hydrogen peroxide solution than can be maintained in the vaporizer, including line 18, the amount of the more dilute hydrogen peroxide supplied to the vaporizer through line 30 always is large enough at any level to dilute the hydrogen peroxide solution circulating through the vaporizer system below 70% by weight. Even though the feed through line 24 decreases or is permanently discontinued, the concentration of the hydrogen peroxide liquid circulating through the vaporizer system is not increased appreciably.

If vaporization is continued, the level falls in the vaporizer and also in the reservoir until at last the level is below the area in the vaporizer which is heated. At this time, vaporization stops. Even before this takes place, however, discharge of liquid in the upper portion of the column through line 14 stops. Slugs of liquid rise up the tube 10 near the outlet into line 14 and then fall back, the vapors proceeding into the separator without substantial liquid. This produces a high degree of surging within the tube 10, pulsations of which are communicated back into header 20 and the pool of reservoir 22. This surging then causes intermixing of the liquid in the vaporizer with the liquid in the reservoir, thus inherently diluting the circulating solution and preventing it from exceeding the explosive concentration.

While this intermixing promotes dilution as described above and has some advantage, it is not absolutely essential and it is desirable to restrict intermixing at least to a degree. This may be accomplished by making pipe 30 relatively long so that surges in pressure created by brief variations in level of liquid in vaporizer 10 are damped in line 30 and do not reflect

an appreciable change in level in the reservoir 22. Alternatively, an orifice may be provided in line 30, or other damping means may be resorted to. Usually, it is advantageous to have the diameter of line 30 substantially less than that of reservoir 22 since this also decreases back-mixing.

In a typical example, an apparatus of the type illustrated in Figure 5.1 was used. The vaporizer was a tube having an internal diameter of 2 inches and a heated height of 120 inches. The jackets 12 terminated 18 1/2 inches above the bottom of header 20. Tube 10 discharged through a one-inch line 14 which, in turn, discharged tangentially into separator 16 which had an internal diameter of 18 inches which, in its bottom section, was free from packing or other obstruction. Separator 16 tapered to a lower section 6 inches in diameter which fed into a one-inch i.d. pipe 18. Reservoir 22, which had an internal diameter of 4 inches, fed into the header 20 through a 4 inch by 1 inch 90° elbow reducer and line 30 which was a one-inch i.d. pipe 18 inches long.

In the operation of the apparatus, an aqueous solution containing 15% by weight of hydrogen peroxide was fed into the reservoir 22, and the system was evacuated to 125 millimeters of pressure. The steam was introduced into the jacket, the temperature within the vaporizer being maintained at about 160° to 165° F. The solution was fed into the reservoir 22 continuously until circulation through the vaporizer began and the system stabilized at a constant level. Thereafter, the feed through line 24 was discontinued. At the time the feed was discontinued, the hydrogen peroxide concentration in the lower portion of the vaporizer was approximately 60% by weight.

Heating was continued by continuing the rate of introduction of steam into jacket 12 at the same rate as before the feed was turned off. Over a period of about 15 minutes, the level of hydrogen peroxide in the vaporizer tube dropped from about 136 inches to 85 inches. During this period, the concentration of hydrogen peroxide in the bottom of the vaporizer rose to 67% by weight; the temperature in the vaporizer rose slightly. In the next 15 minutes, the level of the liquid in the vaporizer fell to about 41 inches and the temperature in the bottom of the vaporizer fell to 96.8° F.

At the end of 34 minutes, the concentration of hydrogen peroxide in the column fell to 55% hydrogen peroxide, due to back-mixing with the hydrogen peroxide in the reservoir. In other runs, the hydrogen peroxide concentration fell to as low as 45% by weight. Thus, as vaporization took place, the back-mixing resulting from the surges produced in the vaporizer caused the hydrogen peroxide solution to become more dilute, and thereby establishment of a hydrogen peroxide concentration in an explosive limit was avoided.

DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER

Müller, J. (48): In the production of highly concentrated hydrogen peroxide according to known processes, hydrogen peroxide of about 30 to 35% concentration is continuously or discontinuously evaporated under vacuum. The pure vapor is then rectified and in order to increase the concentration, heat has also been supplied to the rectification or in connection with such rectification. Another method has also become known in which the peroxide solution is totally evaporated one or more times and the resulting vapors then fractionated to

obtain the desired concentration. All of these proposed processes have the disadvantage that the solutions which have already been brought up to a high concentration must be subjected to a further heating or vaporization in order to increase the concentration. This leads to the danger of losses by decomposition, and furthermore the handling of concentrated hot peroxide solutions in larger quantities is not without danger.

It has now been found that these difficulties can be avoided if the solutions with a concentration of over 70% or 75% are concentrated only by a regulated rectification as the last step, without rendering it necessary to heat or vaporize the highly concentrated products again. Dilute solutions, preferably with a hydrogen peroxide content of about 35 to 45% by weight and lower, are first partially vaporized, preferably in a climbing evaporator, and the resulting vapors are then passed through a dephlegmator connected to the evaporator and contacted countercurrently with a solution of the same hydrogen peroxide concentration as the starting peroxide solution. Advantageously, the same peroxide solution is supplied partly to the evaporator and partly to the dephlegmator in a predetermined ratio, as will be more fully described.

In this way, heat is saved as the reflux is not provided as heretofore by cooling but rather by the fresh starting solution which is concentrated thereby. An already preconcentrated peroxide solution is then withdrawn from the dephlegmator and totally vaporized in a second step in an elevator. The vapors of this step are then passed with high concentration directly to a rectification column, where they are fractionally condensed to the desired concentration with the aid of controlled cooling provided at the head of the column. The highly concentrated product is then directly collected in storage containers, without it being necessary that it be heated again.

A separator is provided between the evaporator of the second step, in which total vaporization takes place, and the fractionating column, in which residues and impurities collect. In continuous operation, this separator must be emptied from time to time.

The concentration of the product of the first step, which is supplied to the total vaporization step, depends upon the extent of the partial vaporization or respectively the amount of the fresh solution supplied to the dephlegmator or reflux. It is consequently possible to control the concentration to a great degree by control of the reflux ratio, and also thereby regulate the concentration effect for the final product.

With a reflux ratio of 0.25 to 0.30 one, for example, obtains a maximum concentration of 93 to 95% by weight in the condensation product of the fractionating column. The concentration attained in the solution, which is supplied to the total vaporization in the second step, is about 70 to 75%. When the final concentrations of only 80 or 85% are desired, it suffices when the concentration of the solution supplied to the total vaporization is only 55 to 45% by weight, and this is easily attained by adjusting the reflux ratio to 1.5 to 1.0.

The smooth progress of the process, and especially the total yield obtained, depends considerably upon the proper carrying out of the total vaporization in the second step. It was found that the proper selection of the material for the construction of the evaporator for the second step is of considerable advantage. The use of an oxidized tantalum tube for such an evaporator gave especially good results. While an anodically oxidized aluminum tube also

could be used, its life is not as long as that of the oxidized tantalum. The oxidation of the tantalum can be effected thermally, but is better effected electrolytically by anodic oxidation in sulfuric acid. The anodic oxidation is carried out until full blocking is effected so that with a voltage of 50 volts practically no passage of electric current can be detected. It was found that tantalum without such oxidation treatment is not entirely stable against concentrated hydrogen peroxide solutions and causes a discoloration of the concentrates, especially when the surface has not been polished. The anodic oxidation therefore replaces a special mechanical preparation of the tantalum surface.

In order to inhibit the passing over of volatile acids during the total vaporization and also in order to provide a proper consistency of the residue, it is advisable to add sodium pyrophosphate to the starting solution until it is neutral to methyl orange. The residue obtained in the total vaporization separates out as a viscous paste so that the danger of clogging is avoided. When aluminum is employed in the apparatus, a small quantity of ammonium nitrate, for example, about 0.1 to 0.3 g./l., can be added to the starting solution to protect the aluminum.

The necessary concentration of the starting solution is effected before the total vaporization, so that upon rectification of the vapor a pure highly concentrated product is obtained directly. The process is therefore characterized in that the direct supply of heat is limited to concentrations at which such heat is still well tolerated. Furthermore, the concentration is effected continuously in such a way that the presence of larger quantities of concentrated and hot peroxide are avoided in the apparatus. Consequently the dangers of handling hot concentrated solutions are reduced to a minimum.

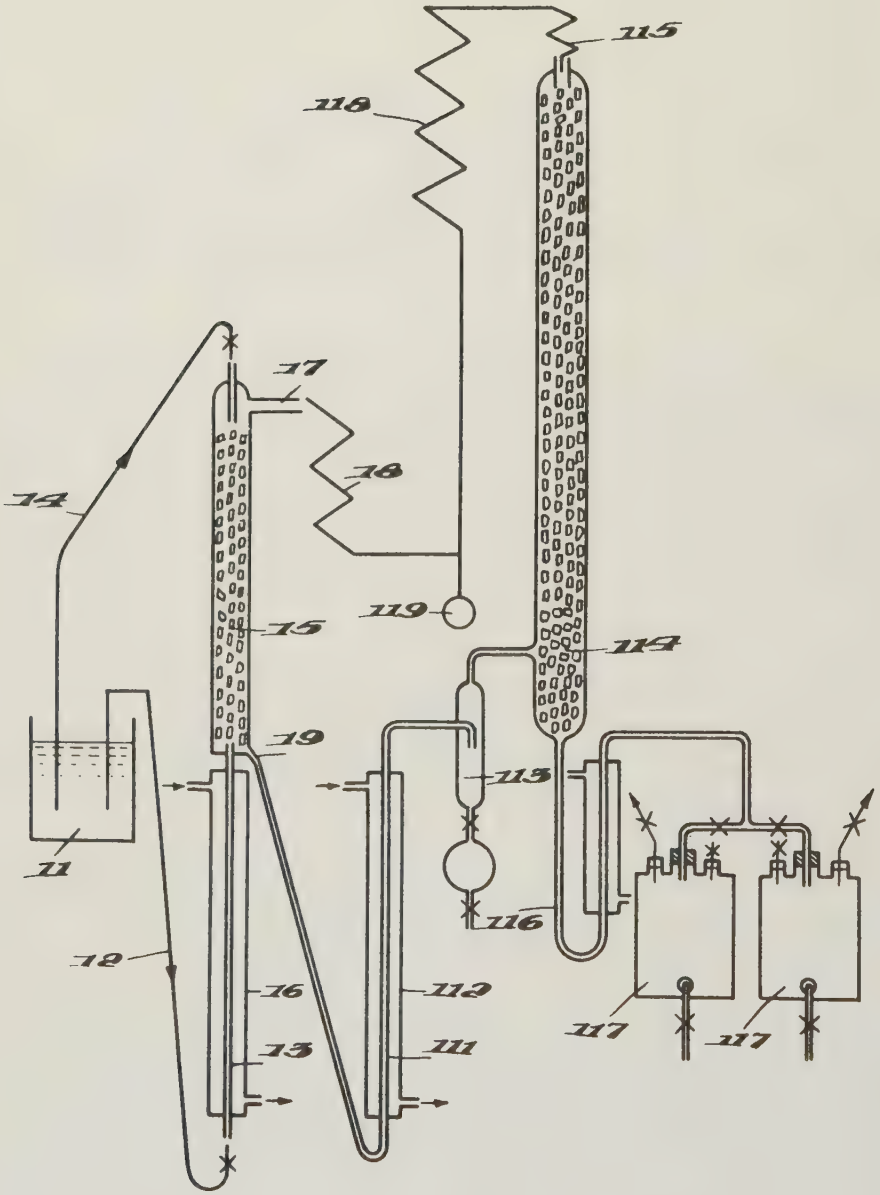
The process is also well suited for the treatment of hydrogen peroxide solutions contaminated with organic components, such as, for example, are obtained with the known anthraquinone process. The volatile organic components are driven off over the head during the concentration, whereas the nonvolatile organic and inorganic components are separated out during the total vaporization, so that a very pure concentrate is obtained.

As the starting solution is employed as reflux during the concentration and the purity of the concentrated product is obtained in a single total vaporization, the process is also very economical to use with relatively dilute starting solutions.

Referring to Figure 5.2, storage vessel 11, for example, contains a 35% hydrogen peroxide solution. Depending upon the desired reflux ratio, a portion of such solution is supplied to evaporator 13 over conduit 12, and another portion to dephlegmator 15 over conduit 14. Evaporator 13 is heated with steam jacket 16 and vapors produced pass into dephlegmator 15, in which they are passed countercurrently to the liquid solution supplied over conduit 14. The excess steam leaves the head of the dephlegmator at 17. When hydrogen peroxide is carried along with such excess steam, this can be returned in dilute form to the hydrogen peroxide production.

A more concentrated hydrogen peroxide solution runs out of the bottom of dephlegmator 15 at 19, preferably over an overflow sill, and is supplied to the total evaporator 111 of the second step. The evaporator 111 is also heated with a steam jacket 112. The vapors leaving the total evaporator 111 are passed through separator 113, in which the impurities are

FIGURE 5.2: DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT PROCESS FOR H_2O_2 CONCENTRATION



Source: J. Müller, U.S. Patent 3,060,105, October 23, 1962

retained and then introduced into rectification column 114 which is provided at its upper end with a reflux cooler 115. This cooler serves to regulate the condensation and is adjusted to provide the desired concentration in the final product.

The concentrate is drawn off over a cooled siphon 116 and is collected and stored in vessels 117. The excess vapors from column 114 are condensed in cooler 118. Coolers 18 and 118 are connected to vacuum pump 119. In order to prevent any contamination and decomposition of the highly concentrated solution, column 114 is preferably constructed of glass and is filled with glass rings or other inert filling bodies. Pure aluminum or oxidized tantalum can also be used for such column, but the latter hardly comes into consideration because of its price. The following is an example of carrying out the process.

10 to 12 liters per hour of a 35% hydrogen peroxide solution were concentrated in an apparatus as in Figure 5.2, in which the heating tubes of the evaporator were 2 meters long with a 20 mm. interior diameter. The quantity of fresh hydrogen peroxide solution supplied to the top of the dephlegmator was such that a reflux ratio of 0.30 was provided. The apparatus was operated under a pressure of 30 to 60 mm. Hg, and the steam employed to heat the evaporator tubes was 0.1 atmosphere gauge pressure.

The temperature reached in the first evaporation step was 55° to 65°C., and the concentration of the liquid peroxide supplied from the dephlegmator to the second evaporator in which total evaporation was effected was 75% by weight. The temperature reached in the second evaporation was 60° to 70°C., and upon condensation of the vapors from the total evaporation a product of 93 to 95% by weight of hydrogen peroxide was obtained. The yield was 98 to 99%, and the highly concentrated product was of very good stability.

FMC CORPORATION

Jenney, T.M., Porter, D.H., and Rice, R.H. (50): It has been found possible to efficiently concentrate aqueous hydrogen peroxide produced by the anthraquinone process at an original hydrogen peroxide concentration of about 15 to 35% to a concentration of about 50 to 80%, and at the same time safely and economically remove essentially all of the carbonaceous impurities in the hydrogen peroxide feed, by heating the hydrogen peroxide solution to vaporize the bulk of the water and hydrogen peroxide, continuously withdrawing from the boiling mixture a residue richer in impurities than the feed, in the amount of 2 to 10% by volume of feed volume and containing not more than about 70% of hydrogen peroxide, separating the vapors into steam and aqueous hydrogen peroxide product having a concentration of about 50 to 80%, passing the steam upwardly through the residue richer in impurities to vaporize and remove from the residue all but 1 to 3% of total hydrogen peroxide originally fed to the system, and discarding a final residue containing the bulk of the impurities in the system and the 1 to 3% of hydrogen peroxide at a concentration of up to about 50% of hydrogen peroxide.

In operation of the process, the feed hydrogen peroxide solution is heated in a purification heater to vaporize the bulk of the solution and provide a mixed vapor of hydrogen peroxide and water, and this vapor is rectified in a first rectifier where it may be concentrated safely to a product containing about 50 to 80% of hydrogen peroxide, while a residue containing

not more than 70% of hydrogen peroxide is removed from the bottom of the purification heater in the amount of about 2 to 10% by volume of the solution fed to this heater, and this residue is passed downwardly through a stripper or rectifier column in which steam from the first rectifier is passed upwardly to strip the hydrogen peroxide from the residue and thereby recover it overhead as an aqueous solution.

A final residue is purged from the bottom of the stripper and contains most of the impurities in the system and about 1 to 3% of the hydrogen peroxide initially fed to the system, this hydrogen peroxide being at a concentration of no more than about 50%. The aqueous hydrogen peroxide solution recovered overhead can be recovered as a product, or can be refed to the purification heater with fresh hydrogen peroxide from the anthraquinone process, and recovered from the first rectifier as a concentrated product, for example, containing about 50 to 80% of hydrogen peroxide.

By this means, essentially all of the hydrogen peroxide fed to the concentration system is recovered safely, and carbonaceous impurities do not reach a concentration in the hydrogen peroxide solutions at which they are a hazard. Furthermore, little or no energy, in addition to that employed to operate the purification heater and first rectification column, is required to recover the hydrogen peroxide from the impurity-containing residue purged from the purification heater, since the steam employed for removing the hydrogen peroxide from this residue is waste steam from the first rectification column.

This process will operate with safety, if, as indicated, at least 2 to 10% by volume of the aqueous hydrogen peroxide solution fed to the concentration system, containing about 10 to 35% of the hydrogen peroxide and essentially all of the carbonaceous impurities, is removed as residue from the purification heater and treated with steam for removal of the hydrogen peroxide.

The carbonaceous impurity level in the feed hydrogen peroxide solution can be as high as about 350 ppm and would rapidly rise in concentration in the purification heater to more than about 10,000 ppm, a concentration at which they render a concentrated hydrogen peroxide solution extremely hazardous, if the residue were not continuously removed. However, in the present process, organic impurities in the 50 to 70% hydrogen peroxide concentrate in the purification heater are maintained below this hazard level.

Furthermore, subsequent stripping of the hydrogen peroxide from the residue from the purification heater, and purging of a final, or stripped, residue in the amount of about 1 to 3% of the amount of hydrogen peroxide fed, keeps the impurity level in the purge below about 20,000 ppm, while at the same time providing a final residue containing not more than about 50% of hydrogen peroxide. This amount of organic impurity, in contact with hydrogen peroxide below 50% in concentration, can be handled safely.

This system is also advantageous in that it permits the residue in the purification heater, comprising organic impurities and hydrogen peroxide, to be purged at high rates. This is due to the subsequent stripping operation during which residual hydrogen peroxide is recovered from the residue before it is discarded as waste. In the absence of a subsequent stripping stage, the purge rate from the purification heater would have to be decreased to prevent loss of excess peroxide with the hydrocarbon impurities. This reduction in the purge

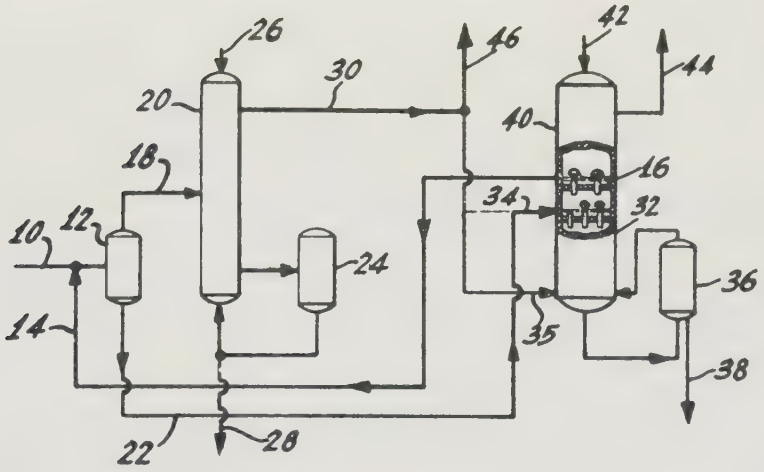
rate is objectionable, since it results in a potentially dangerous buildup of carbonaceous impurities in the purification heater.

Reference has been made to hydrogen peroxide at a concentration of about 50 to 80%. It will be apparent that the hydrogen peroxide can be concentrated to an even higher level than 80% by further heating and rectification steps. The original concentration and purification removes essentially all of the carbonaceous impurities, so that they no longer present a hazard in the system.

The process will now be described more fully with reference to Figure 5.3, which represents a distillation and stripping system.

Aqueous hydrogen peroxide 10 derived from the anthraquinone process and containing about 15 to 35% of hydrogen peroxide, and about 350 ppm of carbonaceous impurities, is fed continuously into the middle of purification heater 12 along with recovered hydrogen peroxide 14 from stripper-enricher 16. The aqueous hydrogen peroxide is heated and vaporized in purification heater 12 at a pressure of about 50 to 100 mm. of mercury, and a residue in the amount of about 2 to 10% of the volume of the solution fed to the heater is continuously withdrawn from the bottom of the heater.

FIGURE 5.3: FMC PROCESS FOR CONCENTRATION OF HYDROGEN PEROXIDE



Source: T.M. Jenney, D.H. Porter, R.H. Rice, U.S. Patent 3,152,052, October 6, 1964

The vapor produced in purification heater 12 is continuously passed through line 18 to a point intermediate the ends of the first rectifier 20, and the residue withdrawn from the bottom of the heater, containing about 10 to 35% of the hydrogen peroxide fed to the system, is continuously passed through line 22 to stripper-enricher 16. The concentration of hydrogen peroxide in the residue send to stripper-enricher 16 is kept below 70%.

The vapors from purification heater 12 are introduced into the middle of the first rectification tower 20, preferably operated at about 30 to 80 mm. of mercury. A primary reboiler 24, preferably operated at about 50 to 100 mm. of mercury, and a source of reflux water 26, are connected to the tower 20. For this operation, aqueous hydrogen peroxide product, having a concentration of about 50 to 80% of hydrogen peroxide, is continuously removed through line 28 from the bottom of rectifier 20, and steam is removed overhead continuously through line 30. The hydrogen peroxide is normally recovered in the amount of about 97 to 99% of the amount fed to the system.

The residue from purification heater 12, moving through line 22, continuously enters stripper-section 32 of stripper-enricher 16 near the top of the stripper-section at 34, and passes down countercurrently to steam derived from rectification tower 20, and introduced through line 30 continuously to near the bottom of stripper-section 32 at 35. The stripper-section is operated at 30 to 40 mm. of mercury. Stripper process solution preferably is passed through reboiler 36, normally operated at about 35 to 60 mm. of mercury, in order to improve recovery of hydrogen peroxide from the solution.

A final residue containing hydrogen peroxide in the amount of about 1 to 3% of the weight introduced into the system, and at a concentration of up to about 50%, is removed continuously through line 38 from the bottom of reboiler 36; this residue may contain up to about 20,000 ppm of carbonaceous impurities, that is, on the order of 99% or more of the organic impurities in the system.

The hydrogen peroxide stripped from the process solution in stripper 32 is then passed continuously upwardly into the bottom of enricher or rectification section 40 of the stripper-enricher 16, where it is rectified, preferably at a pressure of about 20 to 45 mm. of mercury, with the aid of reflux water introduced through line 42, at the top of the rectifier. It will be apparent that the rectifier may be positioned above the stripper, as shown in the drawing, or the two may comprise two separate columns, or other like equipment. In either case, hydrogen peroxide is stripped from the residue in the stripper and passed as a vapor into the enricher column where it is rectified for removal of water from the stream with the aid of reflux water.

Excess steam is removed from the system through line 44 at the top of the enricher, and together with excess steam from primary tower 20, via line 46, is discarded. The hydrogen peroxide recovered from enricher 40 is passed continuously from the bottom thereof through line 14 to join with fresh hydrogen peroxide solution with which it is fed into purification heater 12.

The apparatus employed should be constructed of glass, stoneware, passivated stainless steel, or similar materials which are resistant to hydrogen peroxide and do not decompose it. Likewise, the water used as a refluxing agent should be free of agents such as metal ions which

decompose hydrogen peroxide. Agents such as sodium stannate, dipicolinic acid and the like which are known as stabilizers for hydrogen peroxide, may be added at any point in the system in order to retard decomposition.

In normal operation of the process, the hydrogen peroxide fed to purification heater 12 is a composite of fresh hydrogen peroxide and hydrogen peroxide recovered from enricher 40. The recovered hydrogen peroxide solution 14 is in the amount of about 10 to 35% of the weight of peroxide 10 introduced into the system, and has a concentration of about 10 to 40% of hydrogen peroxide, so that the concentration of the peroxide fed to purification heater 12 has a concentration about the same as that derived from the anthraquinone process, usually about 15 to 35%. The composite peroxide solution contains less impurities than the peroxide coming from the anthraquinone process, the recycle peroxide having been stripped of much of its impurities.

By way of illustration of the process, the following example is given of the concentration and purification of hydrogen peroxide derived from the anthraquinone process, and containing about 20% of hydrogen peroxide, in a continuously operating system.

8,080 kg. of 20.2% hydrogen peroxide from the anthraquinone process, and containing 263 ppm of organic impurities, is passed continuously together with 1,485 kg. of hydrogen peroxide of the same concentration and containing essentially no impurities, recovered from stripper-enricher 16, into a purification heater 12, operated at 40 to 70 mm. Hg absolute and 35° to 70°C. 9,013 kg. of this solution is continuously removed overhead as a vapor containing about 17.7% of hydrogen peroxide, and passed into the middle of first rectification tower 20. A residual aqueous solution from purification heater 12, in the amount of 552 kg., having a concentration of 62% of hydrogen peroxide and 3,840 ppm of carbonaceous impurities, is continuously withdrawn and passed into the top of stripper 32.

The first rectification tower is operated at a pressure of about 50 mm. of Hg absolute, and employs a reboiler maintained at a pressure of about 60 mm. of Hg. Reflux water is passed into the top of the column. Rectification is conducted to permit continuous removal of hydrogen peroxide at a concentration of 70% in the amount of 2,270 kg. from the bottom of tower 20, while steam, containing essentially no hydrogen peroxide, is removed continuously through line 30 at the top of this rectification tower. 552 kg. of 62% hydrogen peroxide solution, containing essentially all of the impurities from the original hydrogen peroxide, is passed continuously into the top of stripper 32, which is maintained at a pressure of about 40 mm. of Hg absolute. It is stripped of hydrogen peroxide by steam passed into the stripper at 34 through line 30 from the first rectification tower 20. Reboiler 36, operated at about 45 mm. of Hg absolute, is employed to assist the stripping operation in stripper-enricher 16.

106 kg. of an aqueous solution containing 40% of hydrogen peroxide, and 20,000 ppm of carbonaceous impurities, essentially all of these impurities introduced into the system with the feed, is continuously removed from the bottom of stripper-reboiler 36 through line 38 and discarded as purge, or final residue, material. The stripped hydrogen peroxide vapor and steam are then continuously passed from the top of stripper 32 into the bottom of enricher 40, maintained at a pressure of about 20 mm. of Hg, and in the enricher they are refluxed with water introduced through line 42. As indicated at the beginning of this example, 1,485 kg. of 20% aqueous hydrogen peroxide is removed during the period of operation

from the bottom of enricher 40, and returned to the hydrogen peroxide feed, line 10, and then to purification heater 12; during the course of being returned, it is brought to atmospheric pressure.

The steam removed overhead from rectification tower 20, in excess of that employed in the stripper, and the steam removed from enricher 40, are raised to atmospheric pressure and continuously removed from the system. Where desired, the purified water derived from the steam is employed as reflux water, thereby avoiding introduction of extraneous impurities.

LAPORTE CHEMICALS LTD.

Banfield, R.H., and MacDonald Hildon, A. (49): The strength of the aqueous hydrogen peroxide obtained from the water extraction stage of the anthraquinone process depends upon many factors, but in any event normally requires concentration if strengths above 25% w./w. H_2O_2 are required. In normal commercial operation, using 2-ethylanthraquinone, the strength of the aqueous solution is often 18% w./w. H_2O_2.

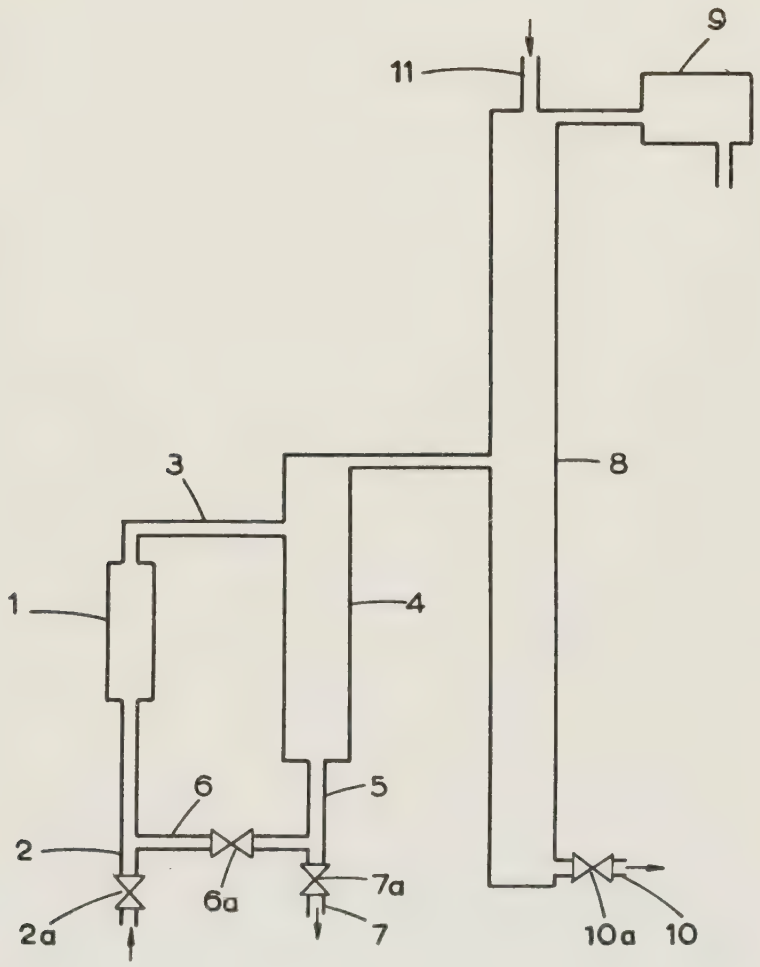
Concentration by fractional distillation requires, according to known techniques, the vaporization of the low strength hydrogen peroxide and the feeding of the vapors obtained to a fractionating column. By the action of such a column, water vapor, low in hydrogen peroxide content with respect to the hydrogen peroxide content of the feed, leaves at the upper end of the column, while aqueous hydrogen peroxide, rich in hydrogen peroxide content of the feed, leaves at the lower end of the column. In such columns, it is usual to introduce, in a known manner, a supply of water as reflux. Similarly, hydrogen peroxide solution derived from the electrolytic process has been concentrated in this manner.

In the past such fractionating columns have been constructed of stoneware, the advantage of which is its extreme resistance to attack by any impurities contained in the lower strength hydrogen peroxide solution fed to the column. However, stoneware columns are extremely heavy, difficult to produce and liable to fracture. Thus an alternative material was sought and high purity aluminum has been suggested as a suitable material. This has many advantages in that it is light and relatively easily worked. The term "high purity aluminum" means material containing at least 99.5% of aluminum by weight.

However, the impurities contained in aqueous solutions of hydrogen peroxide, derived from both the electrolytic and anthraquinone processes, make a general attack upon the surface of the still, resulting in shortened plant life and lowered distillation efficiency, and furthermore, causes appreciable quantities of aluminum to appear in the final product. This is often extremely undesirable in that, for instance, it increases the turbidity, and decreases the stability of the product due to associated traces of iron and copper. Furthermore the dissolved aluminum will often deposit in another unit of the plant with serious consequences.

It is an object of this process to provide means whereby this attack is eliminated or substantially reduced. The concentration of aqueous hydrogen peroxide is effected by fractional distillation in a high purity aluminum column, in which reflux water is added at or near the top of the fractionating column and phosphate ions are present in this reflux water at a concentration of between 10 and 300 ppm.

FIGURE 5.4: LAPORTE CHEMICALS CONCENTRATION PROCESS FOR HYDROGEN PEROXIDE



Source: R.H. Banfield, A. MacDonald Hildon, U.S. Patent 3,073,755, January 15, 1963

Preferably, phosphate ions are initially present in a concentration of at least 200 ppm with respect to the reflux water, but subsequently the concentration may be lowered to not less than 10 ppm.

The phosphate is best added in the form of acid sodium pyrophosphate, $Na_2H_2P_2O_7$. Typical of other suitable salts are potassium pyrophosphate and the salts $M_3HP_2O_7$ and $MH_3P_2O_7$, where M is sodium potassium or lithium. $Na_4P_2O_7$ can be used, but gives rise to an increase in pH which will not be found desirable in all cases.

It will be understood that sufficient reflux water must be added to the fractionating column. The basic relationship is that the total number of mols (H_2O + H_2O_2) issuing from the bottom of the column is the same as the number of mols of water entering as reflux. For example, if 18% w./w. H_2O_2 is fed to a fractionating column producing 66% w./w. with a purge rate of 5% of the feed H_2O_2, an overhead loss of 0.3% and a decomposition of 2.5%, then for every gallon of feed, about 0.2 gallon of reflux water is required.

Referring to Figure 5.4, the crude hydrogen peroxide is fed into the vaporizer 1 through pipe 2, controlled by valve 2a, and then passes by pipe 3 to the entrainment separator 4, in which most of the nonvolatile impurities are removed, the entrained liquid being recycled through pipes 5, 6 (controlled by valve 6a) and 2 to the vaporizer 1. The stream is purged from time to time by removing solution through pipe 7, controlled by valve 7a, to keep the impurity content low. The water and hydrogen peroxide vapors are passed from the entrainment separator 4 and introduced into an intermediate zone of the fractionating column 8.

The rising vapors become depleted in hydrogen peroxide and the resulting overflow from the column is essentially hydrogen peroxide-free water vapor. The falling stream of water becomes progressively richer in hydrogen peroxide and conditions are regulated so that the bottom product from the column which leaves through pipe 10 gives hydrogen peroxide of the required strength.

The overflow from the column is passed into a condenser 9 and reflux water is introduced into the top of the column through pipe 11, the phosphate ions being present in this reflux. Although, as will be seen subsequently, the experimental results of adding the phosphate to the reflux water undisputedly indicate that it protects the aluminum surfaces of the still from corrosion, it is not certain how the protection is effected. It might possibly be effected by the formation of a protective phosphate coating or skin on the surface of the aluminum. The effects of the addition on various factors, both of distillation process and product, will be seen in the following tables.

Effect of Adding Acid Sodium Pyrophosphate to the Reflux Water on the Distillation Efficiency

Grams per litre acid sodium pyrophosphate ($Na_2H_2P_2O_7$)	Distillation efficiency measured in terms of percent of hydrogen peroxide recovered in the product
nil	94.7, 94.9, 94.5, 94.8, 94.8, 94.4, Av.=94.7.
0.1	95.3, 95.1, 95.0, 95.3, 95.1, 95.3, Av.=95.2.
0.2	95.0, 95.3, 95.2, 95.3, 95.2, 95.4, Av.=95.2.

This is a significant and valuable increase in plant efficiency.

Effect of Adding Acid Sodium Pyrophosphate to the Reflux Water on the Total Amount of Stabiliser (Acid Sodium Pyrophosphate) Required to Stabilize the Product

Experiment	Amount of acid sodium pyrophosphate ($Na_2H_2P_2O_7$) added to the reflux water	Amount of extra acid sodium pyrophosphate required to reduce the decomposition rate to 0.12 to 0.15 ml./min. per 25 ml. sample at 100° C.	Total acid sodium pyrophosphate in sample
	G./l.	*G./l.*	*G./l.*
1	0.1	nil	0.1
2	0.1	nil	0.1
3	nil	[1] 0.4	0.4
4	nil	[1] 0.4	0.4

[1] These quantities reduced the decomposition rate to just below the upper limit.

This is a useful improvement, as the solids content of the product is considerably reduced.

Effect of Adding Acid Sodium Pyrophosphate to the Reflux Water on the Rate of Decomposition of the Product

[In both cases acid sodium pyrophosphate was added to the product to bring the final concentration up to 0.25 gram/litre. The figures quoted are rates of decomposition expressed as ml./min. of oxygen evolved from a 25 ml. sample at 100° C.]

No addition of acid sodium pyrophosphate to reflux water	0.1 gram/litre sodium pyrophosphate added to reflux water
0.58	0.19
0.30	0.15
0.29	0.19
0.29	0.15
0.25	----------
0.28	----------
Average 0.33	Average 0.17

This is a very significant reduction in the rate of decomposition

Effect of Adding Acid Sodium Pyrophosphate to the Reflux Water on the Amount of Aluminium in the Product

Time in days	Amount of $Na_2H_2P_2O_7$ added, g./l.	Aluminium in the product, mg./l.
1	nil	5.3
4	nil	14.1
5	0.2	5.4
6	0.2	1.3
7	0.2	1.2
19 to 40	0.1	0.8 to 1.0
47	0.1	0.8
49	nil	4.9
50	nil	16.6
51	nil	22.4
52	nil	24.8
53	nil	24.6

It will be seen that at the time of the first two tests, no pyrophosphate had been added to the reflux, and the aluminum content of the product was high. Between the 4th and 5th day pyrophosphate addition to the reflux was started, and by the 7th day the concentration of the aluminum had dropped appreciably. After the 47th day, the addition of pyrophosphate to the reflux was discontinued; the aluminum content of the product rose sharply.

It will further be seen from the table that once the desired protective effect had been achieved, the quantity of pyrophosphate required to inhibit attack on the aluminum surfaces was much smaller (cf. the 40th day), though if this small quantity was stopped appreciable attack took place (cf. 49th and subsequent days).

Effect of Adding Acid Sodium Pyrophosphate to the Reflux Water on the Rate of Corrosion of Aluminium

[Samples of aluminium were placed in the effluent from the fractionating column of two distillation units operating under identical conditions except than in one unit acid sodium pyrophosphate was added to the reflux water. The rate of corrosion is expressed as milligrams of aluminium dissolved per square decimeter per day (MD^2D)]

Time in Days	Loss of Aluminium MD^2D	
	0.1 g./l. $Na_2H_2P_2O_7$ added to reflux	No. additions to reflux
0 to 8	6.2	27.6
8 to 12	8.4	25.2
12 to 16	9.2	27.1
16 to 20	4.8	26.0
20 to 24	5.4	19.8

Thus, the rate of corrosion in the presence of acid sodium pyrophosphate is reduced by a factor of 3 to 5. This is a very substantial reduction and of great importance, since corrosion of aluminum affects stability because iron is present to the extent of about 0.2% in 99.5% purity aluminum, and iron ions are catalytically active towards hydrogen peroxide decompositions.

Effect of Adding Acid Sodium Pyrophosphate to the Reflux on the Clarity of the Product

Day added	$Na_2H_2P_2O_7$, g./l.	Appearance of product
1	0	Hazy.
4	0	Hazy.
5	0.2	Hazy.
6	0.2	Fairly clear.
7	0.1	Almost clear.
19	0.1	Bright.

In the second experiment the clarity is expressed quantitatively in cms., being the length of a trace on a cathode ray (C.R.) tube.

Day	$Na_2H_2P_2O_7$ added, g./l.	Clarity (Length of trace CR tube)
1	0.1	3.3
8	0.1	2.1
10	0	5.3
14	0	>11.0

In connection with the last two tables, it should be noted that a reference solution, being a 40 g./liter solution of a standard sample of polystyrene (clear granules) in benzene, gave a reading of 3.2 cms. The standard selected is quite arbitrary but reproducible. The method of measuring was as follows.

The solution was placed in a rectangular optical cell and inserted in the cell-holder in a beam of light which converged to a focus just beyond the cell. Light scattered at right angles was received through a microscope objective, the function of which was to direct the light scattered from a small segment of the illuminated field on to the cathode of a photomultiplier valve. The current so produced was converted to a wave form and measured as a linear trace on a cathode ray tube. The combination of microscope objective and cathode ray tube enabled the scattering due to the haze to be separated from that due to passing oxygen bubbles from decomposition of the hydrogen peroxide.

PPG INDUSTRIES

Graybill, W.B. (47): This is a simple and efficient process for obtaining from dilute aqueous hydrogen peroxide solutions highly concentrated aqueous hydrogen peroxide solution containing upwards of 70% and as high as 90 to 95% hydrogen peroxide by weight. It accomplishes these ends on a scale and with the safety and equipment befitting commercial operation. It obviates the need for a multiplicity of distillations and the attendant equipment demands. When conducted under optimum conditions, the process concurrently purifies aqueous hydrogen peroxide solutions, notably by removing carbonaceous impurities.

It has been discovered that aqueous hydrogen peroxide solutions exceeding 70 weight percent hydrogen peroxide strengths may be obtained by charging dilute aqueous hydrogen peroxide of upwards of 8 weight percent hydrogen peroxide content to a liquid body of aqueous hydrogen peroxide at vaporizing temperatures and under vacuum. Vapors of water and hydrogen peroxide are formed, often including entrained liquid. This entrained liquid may be removed, if desired and the vapors are fed into an intermediate section of a liquid-gas contact zone under vacuum. Vapors of a water-hydrogen peroxide composition corresponding to the vapors in equilibrium with an aqueous hydrogen peroxide solution of at least 70% hydrogen peroxide under temperature and vacuum conditions prevailing in the zone are fed to the zone at a point vertically beneath the intermediate point.

Under typical vacuum and temperature conditions prevailing, e.g., 150° to 160°F. and 35 to 50 millimeters mercury pressure, vapor mixtures comprised of from 25 to 70 weight percent hydrogen peroxide and water constitute the feed. Of course, other conditions may alter somewhat the precise vapor composition used.

The effect in the gas-liquid contact zone may be described as a stripping action in which the vapors fed at the lower point preferentially remove water vapors from the zone's contents and become depleted in hydrogen peroxide. Thus, a rising gas stream is present which is progressively richer in water vapor and leaner in peroxide vapors. Countercurrent to the rising gas stream is a downwardly flowing stream which progressively becomes enriched in hydrogen peroxide and depleted of water. This downwards flowing stream is, under the prevailing conditions, a liquid which is subjected to stripping by the rising gas stream.

When the liquid-gas contact zone is packed or otherwise provided with means for facilitating fractionation above the intermediate point, the overhead product withdrawn from the zone is less rich in hydrogen peroxide than either of the feeds. With adequate fractionation in the upper section of these zones, the overhead may be essentially hydrogen peroxide-free water vapors. As will subsequently be more carefully explained, the overhead may be condensed and a portion returned as reflux.

As the descending liquid stream becomes progressively richer in hydrogen peroxide, it approximates or equals the hydrogen peroxide concentration of the liquid which would be in equilibrium with the vapor composition introduced into the lower section of the zone. Since the quantity of concentrated hydrogen peroxide required to generate the necessary vapors for introduction in the lower portion of a zone is but a small fraction of the concentrated hydrogen peroxide which may be collected as underflow from the zone, the overall effect of the process is to obtain large quantities of concentrated hydrogen peroxide aqueous solutions at the expense of only a fraction of the volume of equivalent concentrated peroxide solutions.

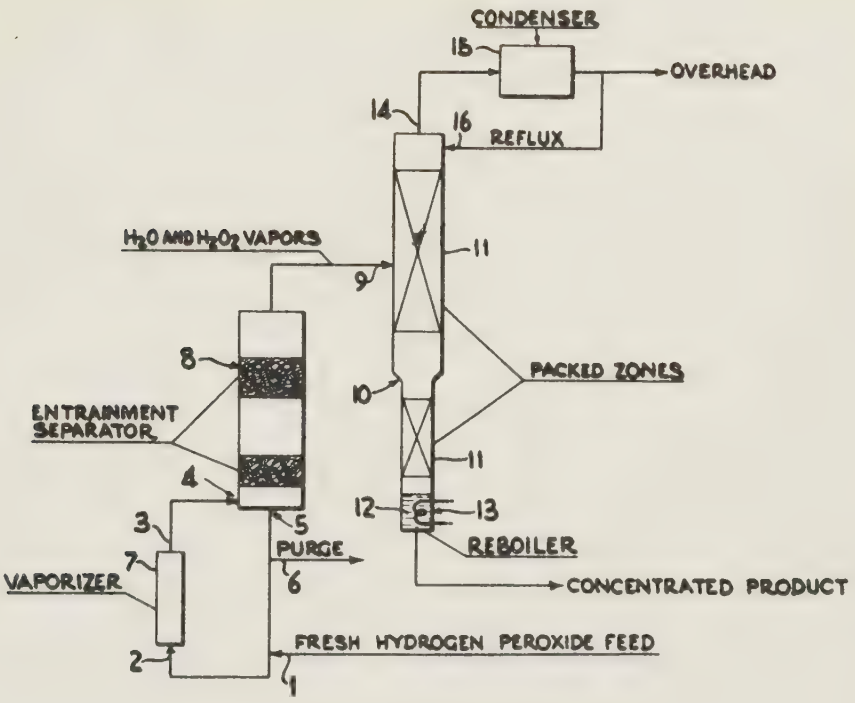
The process involves utilizing the underflow from the liquid-gas contact zone as the direct source for the vapors which are introduced into the lower portion of that zone. This vaporization is accomplished by heating the liquid underflow collected in the lowermost portion of the zone, while it is in liquid-vapor communication with the zone to volatilize a fraction of the underflow as vapor feed to the lower portion of the zone.

This ability to heat directly the underflow and volatilize aqueous hydrogen peroxide solutions of such high strength without undue contamination and hazard represents a marked advance in the concentration of aqueous hydrogen peroxide solutions. It is in part at least the sequential steps described here which apparently are responsible for providing as underflow a highly concentrated aqueous hydrogen peroxide solution of such quality that explosive hazards are substantially minimized, if not precluded.

With reference to Figure 5.5, dilute aqueous hydrogen peroxide ranging from 8 to 16% by weight hydrogen peroxide concentration is fed to the concentration and/or purification system at point 1 in the cyclic arrangement denoted by numerals 1 through 6 inclusive. As it enters this circuit, this dilute hydrogen peroxide solution is admixed with a more concentrated hydrogen peroxide solution. Under most circumstances, the concentration of hydrogen peroxide in the aqueous solution in this circuit is approximately 1.6 to 6.5 times that of this feed concentration but not greater than 83 weight percent. The ratio of the volume of dilute aqueous hydrogen peroxide fed at 1 to the total volume of aqueous hydrogen peroxide in the closed circuit is sufficiently low, so that there is no appreciable decrease in the overall concentration of the aqueous hydrogen peroxide of the circuit. The manner in which the concentration of aqueous hydrogen peroxide in the closed circuit is provided will be fully apparent from the ensuing description.

In this closed circuit, the aqueous hydrogen peroxide solution circulates at a rapid rate in the indicated direction. At point 2 in the circuit, the solution is passed up through vaporizer 7 where heat is supplied. This vaporizer is typically constructed of nickel and may be a thermosiphon vaporizer. This heating volatilizes the material in the system, and the contents of the system are kept in their circulatory motion by the resulting siphon-type effect.

FIGURE 5.5: PITTSBURGH PLATE GLASS CONCENTRATION PROCESS FOR HYDROGEN PEROXIDE



Source: W.B. Graybill, U.S. Patent 2,990,341, June 27, 1961

Observation of the contents of this circuit indicates that the liquid is more in the nature of a boiling body containing vapor bubbles. At 4 in the circuit, the contents spill into the lower portion of entrainment separator 8, where the water and peroxide vapors including entrained liquids rise. Separation of the entrained liquid is facilitated by including zones in the entrainment separator which are comprised of fiber glass or other equivalent materials. The entrained liquid is separated from the water and peroxide vapors and returns to the lower portion of the entrainment separator. There it combines with the material being circulated in the circulatory system.

Emanating from entrainment separator 8 are the water and hydrogen peroxide vapors substantially free from entrained liquid. The hydrogen peroxide content of these overhead vapors from the entrainment separator usually roughly correspond to the concentration of the hydrogen peroxide feed introduced at 1. There may be some slight dilution.

These vapors are then introduced to an intermediate section of a liquid-gas contact column 10. In one specific form of contact column 10, two distinct packed zones 11 are provided. The vapors of water and hydrogen peroxide are introduced into the uppermost of the packed zones. At the lower end of column 10, a liquid body 12 of concentrated hydrogen peroxide is maintained at a concentration corresponding to the desired hydrogen peroxide concentration

in the ultimate product desired. This peroxide concentration is substantially greater than the peroxide content of the vapors introduced at 9. This liquid body 12 is maintained at a temperature corresponding to its boiling point under the pressure conditions of column 10 by heating. Reboiler 13 constitutes this heat-introducing means. The amount of heat introduced into the liquid body 12 is regulated such that but a portion of the liquid body is volatilized to form a rising stream of hydrogen peroxide and water vapors which initially has a composition corresponding to the liquid-vapor equilibrium under the specified conditions.

These vapors gradually rise up through column 10, intimately contacting the water and hydrogen peroxide vapors introduced at the intermediate point 9 of column 10. Below intermediate feed point 9, this rising stream is in intimate contact with a downward flowing liquid stream of water and hydrogen peroxide. It serves the overall effect of stripping water from the zone and ultimately removing water as overhead.

Overhead is withdrawn from column 10 at point 14 and is condensed in condenser 15, with a portion of the condensate recycled as reflux at point 16. The balance is removed from the system as essentially hydrogen peroxide-free water under ideal or near perfect conditions. Small concentrations of hydrogen peroxide may be tolerated in the overhead. Above intermediate point 9, reflux in the packed zone serves to scrub the rising gas stream of hydrogen peroxide and hence to minimize the concentration of hydrogen peroxide in the overhead.

As the water and hydrogen peroxide vapors introduced at intermediate point 9 in effect descend column 10, they form a stream being gradually depleted of water which ultimately collects in the lower portion of column 10 in pool 12. From pool 12, the concentrated aqueous hydrogen peroxide is removed at a rate such that the volume of pool 12 is essentially constant. Heating means reboiler 13 may be directly inserted into liquid body 12.

In conjunction with the concentration of dilute aqueous hydrogen peroxide in the manner described, the present system is preferably operated to effect purification of the hydrogen peroxide. This purification is both important to the quality of the concentrate and also is believed to enhance the overall operation. Impurities of the character concerned are generally termed carbonaceous impurities, and are reported analytically as carbon.

It is observed in the operation of this process that the concentration of carbon (organic impurities) in cyclic system 1 to 6 is considerably higher than the carbon concentration in the aqueous hydrogen peroxide feed introduced at 1. As a result, and to avoid a gradually increasing buildup of carbon concentration in the contents of the cyclic system, the cyclic system is periodically or continuously purged at 6. This purge removes only a small portion of the hydrogen peroxide introduced into the entire system at 1. Generally it is on the order of 1 to 3 weight percent of the feed hydrogen peroxide, but sometimes larger quantities are purged, e.g., 5 to 8 weight percent. When so purging, the overall effect of the entire concentration system described is the production of a concentrated product containing a lower carbon content than the dilute aqueous hydrogen peroxide.

The entire system is operated under subatmospheric conditions, with the temperatures employed in vaporizer 7, reboiler 13 and throughout the rest of the system being to some extent interdependent upon the exact subatmospheric pressure in the system. Pressures used are

below 100 millimeters of mercury. Within the practical limitations of commercial operation, the lowest possible pressure is preferred; this usually is in the range of 30 to 50 millimeters of mercury pressure.

For the most part, temperatures in vaporizer 7 are on the order of 120° to 150°F., and the liquid temperature in pool 12 generated by reboiler 13 ranges on the order of 135° to 155°F., more notably at about 150°F. The following example illustrates the process.

Using a system corresponding to that diagrammatically illustrated in Figure 5.5, 1.25 gallons per hour of aqueous hydrogen peroxide containing 40% hydrogen peroxide by weight and 0.16 gram per liter of carbonaceous impurities measured as carbon was fed to a circulating body of aqueous hydrogen peroxide containing 73.5% by weight hydrogen peroxide and 2.3 grams per liter of carbon. This body of aqueous hydrogen peroxide was circulated as illustrated upward through a nickel vertical vaporizer operated at 144°F. The resulting mixture of water and hydrogen peroxide vapors were passed upward through an entrainment separator, where entrained liquid was separated from the vapors and the essentially liquid free hydrogen peroxide, and water vapors emanating from the separator were fed into the upper section of a liquid-gas contact tower. The vapors at this point contain about 39.1% hydrogen peroxide by weight.

The liquid-gas contact tower was comprised of an upper section 6 inches in diameter and 10 feet high. This section was packed with 3/4 inch Raschig rings. The lower section of the gas-liquid contact tower was 6 feet high and 4 inches in diameter. It was packed with 1/2 inch Raschig rings. A 99.6% pure aluminum finger reboiler was employed to maintain the temperature of the liquid in the reboiler at the lower extremity of the liquid-gas contact tower at 158°F. Overhead from the liquid-gas contact tower was condensed. This condensate was essentially free of hydrogen peroxide. Deionized water was fed to the top of the zone at 0.702 gallon per hour as reflux.

Underflow from the liquid-gas contact tower was removed at the rate of 0.45 gallon per hour and comprised an aqueous hydrogen peroxide solution containing 88.83 weight percent hydrogen peroxide and 0.24 gram per liter of carbon impurities. The entire system was under vacuum, with the vacuum being applied to the upper end of the contact tower. This vacuum was approximately 35 millimeters of mercury pressure. At other points in the system, the subatmospheric pressure was somewhat greater due to pressure differentials.

A purge stream was continuously withdrawn from the liquid body of aqueous hydrogen peroxide which is vaporized into the entrainment separator. This purge stream had a composition corresponding to the composition which is subjected to vaporization. The rate of purge was such that the hydrogen peroxide removed amounted to approximately 5% of the total hydrogen peroxide fed to the system. In this instance, the purge served the purpose of protecting against the buildup of large concentrations of carbon impurities in the purged body.

STABILIZATION

The retardation or prevention of hydrogen peroxide decomposition has been the subject of numerous investigations and studies in recent years. An excellent discussion of theoretical decomposition mechanisms and suggested stabilization agents is presented in the American Chemical Society Monograph No. 128, "Hydrogen Peroxide", by W.C. Schumb et al (74).

From a theoretical viewpoint, it appears that the tendency of absolutely pure hydrogen peroxide to decompose into water and oxygen is negligible. This appears to be true even if the pure material is in aqueous solution, provided that the water of solution is absolutely pure. However, in practice numerous agents or conditions tend to initiate or accelerate decomposition. Thus, a very slight trace of dissolved impurity such as ferric or other metallic ions exerts a marked catalytic decomposition effect. It also appears that the surface of the container in which the hydrogen peroxide is placed has a significant influence on decomposition rates. For example, a rough container surface or the presence of minute surface scratches will increase decomposition rates to an extent which will vary in an empirical manner dependent upon individual circumstances. Temperature and pH also influence decomposition tendency to some extent.

In commercial practice it is, therefore, usually necessary to provide small amounts of an additive to act as stabilizing agents for hydrogen peroxide solutions containing up to 30% to 40% hydrogen peroxide. This is particularly necessary in the case of the more dilute solutions, that is solutions containing less than 3% hydrogen peroxide, since the decomposition tendency of a dilute aqueous hydrogen peroxide solution is considerably greater than that of a concentrated solution, all other factors being equal.

In many commercial processes, large quantities of hydrogen peroxide are utilized in dilute solutions as bleaching agents and similar purposes; the textile industry alone generally accounts for one-third of all hydrogen peroxide consumed in non-military usage. In textile usage, various additives are usually incorporated in the dilute hydrogen peroxide solution for other purposes relating to the processing of cloth. While it has been indicated that cloth processing additives such as sodium silicate also produce a stabilizing effect in textile bleach solutions, it has been found nevertheless in many cases that decomposition of the hydrogen peroxide in bleach solutions represents a considerable economic loss.

In addition to the use of stabilizing agents, rather specific materials of construction are required for hydrogen peroxide containers. As indicated in Schumb et al, p. 524, cited supra, boro-silicate glass, aluminum, tin, magnesium and certain stainless steels have been

found to exert a minimum catalytic effect on the decomposition process. Thus these are the preferred materials of construction for hydrogen peroxide containers. Usually an additional surface conditioning procedure is applied to the container, in order to further reduce its surface decomposition effect.

Among the various stabilizing agents which have been employed in practice may be mentioned sodium stannate, 8-hydroxy quinoline and sodium pyrophosphate. In some cases a combination of two or more agents has been found to provide more effective protection than any one taken singly. Thus, by combining agents, a total reduction in decomposition rate is achieved which may be greater than the sum of the individual reductions which result when the agents are used independently. The selection of a combination of this nature is usually determined by mere experimentation, since it is an empirical phenomenon which depends on individual circumstances such as conditions of hydrogen peroxide storage and usage, and type of contamination and nature of contaminant which may be encountered.

For certain purposes limitations may be placed upon the choice of an inorganic stabilizer due to the quantity of undesirable residual matter which may be left after a large quantity of the hydrogen peroxide has been decomposed in use. Another important consideration which applies particularly to organic stabilizing agents is the matter of stabilizer unit cost relative to the amount of stabilization achieved. Some organic agents are not acceptable in cases where prolonged storage of the hydrogen peroxide solution prior to use may take place, since under such circumstances slow oxidation may destroy the effectiveness of an organic compound. In this section a comprehensive review of both organic and inorganic stabilizing agents will be made.

NITRILOTRIACETIC ACID

PPG Industries (Columbia-Southern); Johnston, P.R. (64): It has been found that hydrogen peroxide may be stabilized effectively by the addition of a small amount of nitrilotriacetic acid. This material has the general formula $N(CH_2COOH)_3$. The amount of nitrilotriacetic acid which can be used normally ranges from about 0.001 to 1% by weight. Normally, the amount used is in excess of about 25 parts by weight per million parts of hydrogen peroxide solution, and the best results usually are achieved when the amount is in the approximate range of 100 to 500 parts of the nitrilotriacetic acid per million parts by weight of hydrogen peroxide solution.

Solutions of any convenient hydrogen peroxide content may be stabilized in this way. However, for most purposes, hydrogen peroxide solutions containing from 10 to 80% by weight of H_2O_2 are so stabilized. While hydrogen peroxide solutions containing 90% or more by weight of H_2O_2 may be stabilized using this material, it is rather common to use such concentrated hydrogen peroxide solutions without stabilizers.

ASCORBIC ACIDS

Chemical Construction Co.; Warshaw, A. (65): It has been found that ascorbic acids are highly effective as stabilizing agents for hydrogen peroxide. The ascorbic acids possess

numerous advantages as compared to other additives previously suggested. They are nontoxic and hence are suitable and advantageous when the hydrogen peroxide is to be utilized for medicinal purposes or in foods. Furthermore, ascorbic acids, particularly the common l-ascorbic acid, are efficient stabilizers for the relatively dilute solutions often encountered in medical practice as well as for more concentrated solutions.

Ascorbic acid is quite inexpensive for this purpose, since relatively small amounts are required for effective stabilization. Additionally, ascorbic acid does not leave an undesirable residue as compared to inorganic agents. Hydrogen peroxide solutions stabilized with ascorbic acid have been found to retain activity and concentration, with negligible decomposition, over long periods of storage. Surprisingly, it has been further found that small additions of ascorbic acids will stabilize hydrogen peroxide solutions even when the solutions are maintained at temperatures approaching the boiling point of water under normal conditions.

SUBSTITUTED 8-HYDROXYQUINOLINES

Shell Oil Co.; Meeker, R.E. (66): Hydrogen peroxide is stabilized by 8-hydroxyquinoline substituted in the 2-position by a saturated hydrocarbon radical. It is surprising to find that 8-hydroxyquinolines, which are substituted in this way, have a long effective life as a hydrogen peroxide stabilizer, since the unsubstituted 8-hydroxyquinoline has an impractically short inhibitor life, especially at the elevated temperatures at which peroxide inhibitors are normally tested to determine their usefulness.

It is believed that the superiority of the new inhibitors is due to the protection which the substituent in the 2-position provides against oxidative attack by the hydrogen peroxide on the quinoline nitrogen atom in the molecule. The substituents used in the inhibitors provide a selective protection of the cyclic amine group, sharply retarding its rate of oxidation to N-oxide without interfering with the effectiveness of the inhibitor as a hydrogen peroxide stabilizer.

A variety of saturated hydrocarbon groups can be substituted in the 2-position of the new inhibitors. Saturated aliphatic or cycloaliphatic or alicyclic hydrocarbon are all useful. Thus one can advantageously use 8-hydroxyquinolines substituted in the 2-position by alkyl, cyclohexyl, cyclohexylalkyl, alkylcyclohexyl or like radicals. The substituent used to shield the nitrogen atom should not be so bulky, however, as to interfere sterically with the ability of the compound to complex with metal ions, since the effectiveness of the inhibitor as a peroxide stabilizer is then decreased. Hydrocarbon substituents in the 2-position having 1 to 9 carbon atoms can be used, but most advantageous as a rule are those with 1 to 6 carbon atoms. The substituent in the 2-position can be linked to the 8-hydroxyquinoline structure at another position as well, as is the case with 10-hydroxy-2,3,4,5-tetrahydroacridine and related compounds, for instance; but as a rule, it is most advantageous to use 8-hydroxyquinolines which have as a substituent a saturated hydrocarbon radical linked to the ring only at the 2-position.

Other substituents can be present in the 2-substituted-8-hydroxyquinolines to be added to the peroxide. For example, it is sometimes desirable to sulfonate the stabilizer to improve

its solubility in aqueous stock solutions and in the H_2O_2 solution to be stabilized. Such sulfonation is especially helpful if the substituent is a large hydrocarbon group which otherwise limits the solubility of the stabilizer in aqueous solutions. An example of such a sulfonated stabilizer is 2-amyl-8-hydroxyquinoline-5-sulfonic acid.

Most advantageously the other substituents, if any, on the 2-saturated hydrocarbyl-8-hydroxyquinoline are also oxidation resistant, since consumption of hydrogen peroxide in oxidation of the other substituent or substituents is then avoided. However, since it is usually necessary to use only very small amounts of the new peroxide inhibitors, the loss of peroxide in oxidation of oxidizable substituents will be negligible. On this account one may use 8-hydroxyquinolines which have in the molecule one or more substituents which react with hydrogen peroxide. It is only important, in other words, to have present in the peroxide being stabilized, a compound having the 8-hydroxyquinoline ring structure with a saturated hydrocarbon substituent in the position alpha to the ring nitrogen.

Ordinarily about 1 to about 250 milligrams of the 2-saturated hydrocarbyl-8-hydroxyquinoline, or mixture of such quinolines, per liter of the hydrogen peroxide being stabilized, is adequate to stabilize the peroxide against excessive loss by decomposition during storage, transportation or use. In some cases, however, larger amounts up to about 1,000 milligrams per liter of peroxide may be useful. Amounts of the order of about 25 to about 150 milligrams per liter will usually be optimal.

PHYTIC ACID

Shell Oil Co.; Dunlop, A.K., and Meeker, R.E. (67): In this process, H_2O_2 is stabilized by phytic acid, i.e., the hexaphosphoric acid ester of hexahydroxycyclohexane, or its soluble salts. It has been found that these compounds are effective in stabilizing percompounds generally, and especially those which present difficult stability problems resulting from contamination of the peroxide with iron.

Only a relatively small amount of phytic acid need be used in the process, amounts of the order of about 1 to about 1,000 milligrams per liter of the solution of percompound being stabilized being usually sufficient. However, larger or smaller amounts, advantageously amounts between about 10 to about 500 milligrams per liter, can be used with good results. The phytic acid can be incorporated in the peroxy compound in any suitable way. For example, in stabilizing aqueous solutions of peroxy compounds one can conveniently add the commercially available 70% phytic acid solution directly to the solution, or a diluted solution of phytic acid in water or peroxide can be added to the solution being stabilized.

There are special advantages in maintaining acidic conditions during stabilization of percompounds with phytic acid, and a pH of about 2 to 5 is preferred when stabilizing hydrogen peroxide, for example. The pH's referred to here are the aqueous equivalent pH's of the peroxide solution which correspond to glass electrode readings in hydrogen peroxide solutions, corrected as pointed out by J.R. Kolczynski et al in Journal of the American Chemical Society, vol. 79, p. 531 (1957).

WATER-SOLUBLE ORGANIC CHELATING AGENT IN PRESENCE OF ALUMINUM COMPOUND AND SOLUBLE PHOSPHATE

Shell Oil Co.; Luten, D.B. Jr., and Meeker, R.E. (68): It has been found that hydrogen peroxide can be stabilized against decomposition during storage transportation and use by means of a special type of water-soluble organic chelating agent, provided there is also present a soluble aluminum compound and a soluble phosphate. By "soluble compounds" is meant compounds having a solubility in water at about 15°C. of at least 10 parts per million.

The water-soluble organic chelating agents which are used in the process are those which have in their molecule at least one trivalent nitrogen atom to which at least two carboxyl groups are attached, the carboxyl groups being each linked to the nitrogen atom by a saturated aliphatic hydrocarbon group of not more than two carbon atoms. The carboxyl groups in these compounds can be in either the free acid form or in the form of salts. In other words, the chelating agents used are those which contain at least one N,N-dicarboxyalkylamino group, $N—(R\cdot COO\cdot X)_2$, where R is an alkylene radical of up to two carbon atoms and X is hydrogen or a salt-forming cation such, for instance as an alkali metal or alkaline earth metal or ammonium ion, the two indicated X's being the same or different.

U.S. Patent 2,371,623 describes a number of chelating agents of this kind which can be successfully used, together with a soluble aluminum compound and a soluble phosphate, in the new compositions. Especially advantageous are those chelating agents which contain a number of N,N-dicarboxyalkylamino groups in the molecule, especially those having at least two adjacent carbon atoms to each of which is directly attached at least one N,N-dicarboxyalkylamino group. Robert E. Meeker, in a previous patent application, described a particularly suitable subgroup of compounds of this preferred type, namely, the water-soluble N,N-dicarboxyalkylamino-substituted carbocyclic compounds having a saturated carbocyclic ring with at least two adjacent ring carbon atoms each directly linked to the nitrogen atom of an N,N-dicarboxyalkylamino group containing up to two carbon atoms in each of the alkyl radicals.

Typical of the hydrogen peroxide stabilizers of this type which are described are the water-soluble 1,2-diaminocycloalkane-N,N,N',N'-tetraacetic acids and their salts having 5 to 18 carbon atoms in the cycloalkane radical, such as 1,2-diaminocyclopentane-N,N,N',N'-tetraacetic acid, disodium 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, tetrapotassium 1,2-diaminoperhydronaphthalene-N,N,N',N'-tetraacetic acid, triammonium 4,7-diisobutyl-1,2-diaminoperhydronaphthalene-N,N,N',N'-tetraacetic acid and the like. By the present process, the effectiveness of these stabilizers can be increased and other types of water-soluble chelating agents, having at least one trivalent nitrogen atom to which at least two carboxyl groups are directly attached, these carboxyl groups being each linked to the nitrogen atom by a saturated aliphatic hydrocarbon group of not more than two carbon atoms, can be made effective stabilizers for hydrogen peroxide.

An especially useful type of such other chelating agent which can be used is the water-soluble alkylene polyamino polycarboxylic acids, having up to three carbon atoms in the carboxylic acid groups, and their salts. Examples of these are: ethylenediamine-N,N,N',N'-tetraacetic acid, which is sold by Geigy Chemical Corporation under the trade name Sequestrene and its tetrasodium salt sold by Dow Chemical Company as Versene;

1,2-diaminopropane-N,N,N',N'-tetraacetic acid; 1,3-diaminopropane-N,N,N',N'-tetrapropionic acid; 1,2-diaminobutane-N,N,N',N'-tetraacetic acid; 2,3-diaminobutane-N,N,N',N'-tetraacetic acid; and the like and their soluble mono-, di-, tri- and tetra-alkali metal, alkaline earth metal and ammonium salts. Representative examples of aromatic polyamino polycarboxylic acids which can be used as such or in the form of water-soluble salts are: ortho-phenylenediamine-N,N,N',N'-tetraacetic acid; 3,4-diaminobiphenyl-N,N,N',N'-tetraacetic acid; 1,2-diaminoanthracene-N,N,N',N'-tetraacetic acid, 1,2,3-triaminobenzene-N,N,N',N',N",N"-hexaacetic acid, and the like. All of these compounds can be produced by reacting the corresponding amines with halocarboxylic acids, using the method of U.S. Patent 2,130,505 for example.

The soluble phosphate compounds which can be used with the chosen polycarboxyalkyl amine chelating agent and aluminum compound can be any of the numerous phosphates which form complexes with heavy metal ions in aqueous solutions. Orthophosphates, and metaphosphates, for example, can be used. However, the polyphosphates such as the pyrophosphates, the polymetaphosphates, particularly the hexametaphosphates, the tri-polyphosphates and the tetraphosphates, for instance, offer special advantages.

The soluble phosphates are preferably added in the form of their salts, the alkali metal salts, especially the sodium and potassium salts, being particularly useful because of their availability and low cost, although ammonium or other soluble salts can be employed, as can the corresponding free acids. Salts corresponding to complete or partial neutralization of the acid, for instance, secondary salts such as Na_2HPO_4 or tertiary salts such as Na_3PO_4 can be added to the hydrogen peroxide in making the compositions. Instead of inorganic salts one can use amine salts or phosphate esters of any of the previously indicated phosphorus-containing acids, although as a general rule these are more expensive and offer no compensating advantages.

A variety of soluble aluminum compounds are also available for the preparation of the new compounds. As a general rule, inorganic aluminum compounds will be used rather than organic compounds because of the tendency of the latter to cause loss by reaction with the hydrogen peroxide. There may be special circumstances in which such reaction may not be unduly detrimental considering the advantage to be obtained from the resulting dissolved aluminum. In such cases an organic aluminum compound can be added. This is especially the case with highly dilute hydrogen peroxide, for example 3 to 6% solutions intended for medicinal applications for instance, which are not such powerful oxidation agents as the more concentrated solutions.

With such solutions, addition of certain types of organic aluminum compounds may have advantages for special purposes. Examples of organic aluminum compounds which can be used are: aluminum di- and tri-acetates, aluminum lactate, aluminum benzoate, aluminum salicylate, aluminum sulfanilate, aluminum benzene sulfonate, aluminum barbiturate, and the like. As a rule, however, inorganic aluminum compounds will be more advantageous, both because of their generally lower cost and more ready availability and because of their greater resistance to reactions which lead to hydrogen peroxide loss. The chosen aluminum compound should be substantially free from heavy metals whose ions catalyze hydrogen peroxide decomposition, whether such metals are present as components of or impurities in the aluminum compound. Because of the greater stability of hydrogen peroxide under acid or

neutral conditions, aluminum compounds which form solutions in hydrogen peroxide having a pH not greater than about 8 are generally preferred, to those which form solutions of higher pH, although the latter may be useful under certain circumstances. Representative examples of suitable aluminum compounds are: aluminum sulfate, the sodium, potassium and ammonium alums, aluminum nitrate, aluminum bromate, aluminum chlorate and the like.

The dissolved aluminum will form a complex with the polycarboxyalkyl amine chelating agent and it may be added to the hydrogen peroxide in the form of such a complex which can be separately prepared, using the stoichiometric proportions of any one or more of the foregoing aluminum compounds with the chosen chelating agent or mixture of such agents, or an excess of either of these components. However, as a general rule it will be simpler to add the aluminum compound and chelating agent to the hydrogen peroxide without preforming the complex. However, the formation of a complex of aluminum ion with the polycarboxyalkyl amine chelating agent is believed to explain in part the advantage of this stabilizer mixture over the prior hydrogen peroxide stabilizers.

STANNATE/POLYCARBOXY AMINE MIXTURE

Shell Oil Co.; Meeker, R.E. (69): An example of a stabilizer mixture within the scope of this process is a sodium stannate/EDTA mixture. Hydrogen peroxide can be stabilized with a mixture of a stannate and one or more water-soluble polycarboxy amines, which have at least one amino nitrogen atom to which is linked two carboxy groups directly joined to the nitrogen atom by saturated aliphatic hydrocarbon groups of one to two carbon atoms, and/or soluble salts of these polycarboxy amines. A special feature of the process in one of its more specific modifications comprises the use of the synergistic combination of hydrogen peroxide stabilizers with a phosphate to obtain still further improved results.

IMPROVED STANNATE STABILIZER

Shell Oil Co.; Meeker, R.E. (70): An important object of this process is to provide a stock solution of stannate stabilizer, which can be admixed simply and inexpensively with a large volume of hydrogen peroxide, to provide both the correct amount of stabilizer and the correct acidic pH for optimum stabilization in one operation, without need for careful adjustment and trimming of the pH of the entire peroxide solution.

In the process, hydrogen peroxide is stabilized by an aqueous solution of a complex of a soluble stannate and a complexing agent for tin in which the concentration of stannate, calculated as $Na_2Sn(OH)_6$, is about 0.05% to about 10% by weight, and the mol ratio of complexing agent to tin is between about 0.5:1 and about 20:1, the solution of the complex having been acidified to a pH below 5, preferably to about pH 1 to 4. Sufficient of this stock solution of acidic complex stannate is added to the hydrogen peroxide to introduce about 0.5 to about 200 milligrams of stannate, again calculated as $Na_2Sn(OH)_6$, per liter of peroxide solution and to make the aqueous equivalent pH of the mixture about 1 to about 5. By this method of operation the stock solution not only supplies the required amount of stabilizer, but also imparts to the peroxide any desired specific pH, preferably one between about 1 and 5, at which the stabilizer mixture is most effective. This is accomplished by

simple mixing of the acidified stannate complex and peroxide solutions, without need for pH adjustment on the peroxide. In preparing the stock solutions of acidic complexed stannate, one can use any of the soluble stannate stabilizers of hydrogen peroxide. Ammonium stannate, the alkali metal stannates and the soluble alkaline earth metal stannates are all useful. Sodium, potassium and magnesium stannates are examples of useful stabilizers which can be employed.

It is essential that a complexing agent for tin be used in the indicated proportions with the chosen stannate or mixture of stannates in preparing the stock solution of stabilizer. Only in this way can the required acidification of the stannate solution to below pH 6 be carried out without massive irreversible precipitation resulting in stannate which is a relatively poor stabilizer for hydrogen peroxide. This undesirable form of stannate precipitate does not readily redissolve when the stock solution is added to the peroxide. It is to be avoided in preparing the stock solutions which may, however, contain reversible precipitates of stannate which redissolve on addition of the stock solution to the peroxide being stabilized. Another advantage of the stock solutions of this process is that, because of complex formation, the stannate and complexing agent are more soluble jointly than separately; so more concentrated solutions can be used without danger of difficulties from undissolved solids.

A variety of soluble complexing agents for tin can be used in preparing the stock solutions of stannate stabilizers. Both organic and inorganic complexing agents for tin, which are stable to hydrogen peroxide, can be used. A number of these complexing agents have a stabilizing effect of their own on hydrogen peroxide and thus offer special advantages over other types of tin complexing agents which are not so effective in this respect, although they may be just as useful in achieving the complexing of the stannate required for the stock solutions.

Among the useful organic complexing agents for tin are, for example, the chelating agents such as the amino carboxyl compounds, for instance, those containing at least one N,N-dicarboxyalkylamino group, $N-(R\cdot COO\cdot X)_2$ where R is an alkylene radical of up to two carbon atoms and X is hydrogen or a salt-forming cation such, for instance, as an alkali metal or alkaline earth metal or ammonium ion, the two indicated X's being the same or different. U.S. Patent 2,371,623 describes a number of polycarboxy amines of this kind such as nitrilotriacetic acid, aminoethyl-N,N-diacetic acid, ethylenediamine-N,N,N', N'-tetraacetic acid, etc., which can be successfully used in the stock solutions. Especially advantageous are those polycarboxy amines which contain a number of N,N-dicarboxyalkylamino groups in the molecule, especially those having at least two adjacent carbon atoms to each of which is directly attached at least one of the N,N-dicarboxyalkylamino group.

The importance of not combining the stannate with the chelating agent in stock solutions until after the stannate has been partially polymerized is shown by the following results of tests carried out with stock solutions made by dissolving 0.1% wt. $Na_2Sn(OH)_6$ in water with and without chelating agent for tin, particularly 1.1% wt. $Na_4P_2O_7$, and then subjecting the solution to treatments effective for polymerization in the absence of the added chelating agent, after which the chelating agent was added to the solutions in which it was not already present and the pH was adjusted to about 3. Aliquots of the stock solutions were diluted 100-fold with 35% wt. hydrogen peroxide containing as impurities 0.1 mg.

iron and 0.02 mg. of copper per liter. The resulting solutions containing 100 mg. of $Na_2Sn(OH)_6$ and 110 mg. of $Na_4P_2O_7$ per liter were tested for stability by heating at 100°C. (See Table 6.1).

TABLE 6.1: H_2O_2 DECOMPOSITION RATE AT 100°C., PERCENT PER 24 HOURS

Method of Stannate Polymerization	Chelating Agent Present during Stannate Treatment	Chelating Agent added only after stannate treatment
Aging 20 days	40	0.8
Acidifying to pH 5	12	0.6
Heating 2 hours at 80° C	14	0.6

It will be seen that the process offers many advantages and is capable of various modifications.

Other stabilizers involving the use of organic chelating agents, with or without admixture, with stannate and phosphate have been described in U.S. Patent 2,961,306 (76) and 3,122,417 (77).

DICARBOXYALKYLAMINO-SUBSTITUTED POLYAMINE PARTIAL SALTS

Shell Oil Co.; Meeker, R.E. (71): A wide variety of N,N-dicarboxyalkylamino-substituted polyamine partial salts can be used as stabilizers for H_2O_2. Their saturated carbocyclic rings can be single or fused rings which can be substituted or not. Particularly useful partial salts are those having the dicarboxyalkyl-substituted amino groups linked to adjacent ring carbon atoms of single saturated hydrocarbon rings of 4 to 9 carbon atoms. Partial salt stabilizers having the dicarboxyalkyl amino groups linked to the carbon atoms of a fused-ring structure advantageously have from 7 to 20 carbons in the fused rings.

Typical examples of unsubstituted acids whose partial salts are useful stabilizers are, for example, the cycloalkane compounds: 1,2-diaminocyclobutane-N,N'-tetrapropionic acid; 1,2-diaminocyclopentane-N,N-tetraacetic acid; 1,2-diaminocycloheptane-N,N'-tetra-acetic acid; and 1,2-diaminocyclononane-N,N'-tetraacetic acid. Representative of the new partial salt stabilizers having fused cycloalkane rings are those of acids such as 2,3-diaminodecahydronaphthalene-N,N'-tetraacetic acid; 2,3-diaminoperhydroanthracene-N,N'-tetraacetic acid; 2,3-diamino-1,4-methanocyclohexane-N,N'-tetraacetic acid; and the like. U.S. Patent 2,519,708 describes methods which are suitable for making these acids.

The new partial salt stabilizers may be used alone or in combination with any of the other known inorganic or organic stabilizers of hydrogen peroxide. Thus the usual stabilizer formulations including pyrophosphate, orthophosphate, stannate, nitrate and the like can be employed with the new stabilizers. One especially advantageous method comprises use of the new stabilizer in the free acid form together with sufficient of a basic reacting

stabilizer such as sodium pyrophosphate or the like to give the desired pH. In this way the total residue in the peroxide solution can be minimized, because the only substances added to the peroxide are active stabilizers. In contrast, in the usual stabilizer formulation using pyrophosphate or stannate or both, all the stabilizers are alkaline and are neutralized with an acid such as phosphoric acid, which adds to the residue but which itself has little or no stabilizing ability. Hydrogen peroxide of any concentration can be stabilized with the new partial salt stabilizers, good results being obtained with H_2O_2 of about 1% to about 90% weight concentration or higher. The following example illustrates the superiority of the new stabilizers over the conventional formulation of inorganic stabilizers.

A sample of 35% weight hydrogen peroxide was stabilized with 110 mg. per liter of sodium pyrophosphate $Na_4P_2O_7$, plus 26 mg. per liter of sodium stannate $Na_2Sn(OH)_6$, and 30 mg. per liter of sodium nitrate $NaNO_3$. The apparent or direct reading pH was adjusted to 2.5 with phosphoric acid, and the sample was stored in a 30-gallon aluminum drum. After several weeks at ambient temperature, the decomposition rate of aliquots of the peroxide as measured by the usual oxygen evolution method had increased from less than 2% per day (24 hours) at 100°C. to 33% per day at 100°C. Fifty milligrams per liter of 1,2-diamino-cyclohexane-N,N'-tetraacetic acid was added to an aliquot and converted to the partial ammonium salt with readjustment of the apparent pH to 2.5 with NH_4OH. This reduced the decomposition rate to 1.1% per day at 100°C., and maintained this low decomposition rate throughout an extended test period of two weeks at 100°C.

DIGLYCOLIC ACID

Solvay & Cie.; Ryckaert, A., and Domen, C. (72): According to this process aqueous hydrogen peroxide solutions of any concentration found commercially, that is to say 3 to 90% by weight, are stabilized by adding minor amounts of an acid of the formula:

$$HOOC-CH_2-Y-CH_2-COOH$$

in which Y represents oxygen or sulfur. Not only are the acids soluble in water and in very concentrated solutions of hydrogen peroxide, but they also resist the oxidizing action of the hydrogen peroxide.

Commercial hydrogen peroxide is, therefore, treated with a sufficient proportion of the specified type of acid to obtain the desired degree of stability. The amount of acid to be added depends on several factors, such as the quality and the initial concentration of the hydrogen peroxide solutions to be stabilized, the desired degree of stability and the use to which the product is to be put.

The acids of the specified type are excellent stabilizers when used alone. They, can, nevertheless, be used in mixtures or even combined with other well known stabilizers for hydrogen peroxide, such as phosphoric acid or phosphates soluble in water. They can also be applied in the form of their water soluble salts. To determine rapidly the quality of the aqueous solutions of hydrogen peroxide, the commercial specifications provide that the determination of stability of these solutions is effected at 100°C. The technique adopted

in the experiments described in the following table consists in measuring, at the given temperature and under known pressure conditions, the volume of oxygen released. From these factors, the quantity of hydrogen peroxide decomposed is calculated on the basis of the reaction:

$$H_2O_2 \longrightarrow H_2O + 1/2\ O_2$$

The results are expressed in grams of hydrogen peroxide decomposed per kilogram of hydrogen peroxide and per hour at 100°C. The concentration of hydrogen peroxide in the starting solutions are expressed in percent by weight. For all the experiments, the vessels containing the samples were new Pyrex glass vessels, passivated by treatment with analytically pure fuming nitric acid, then rinsed several times with bidistilled water and finally dried in a desiccator.

Stabilizers Nature	Amount used; in mg./kg. 110% H_2O_2	Decomposition in g. H_2O_2 decomposed/kg. 100% H_2O_2/h. at 100° C., for solutions of H_2O_2 at—		
		10%	35%	70%
	0	>200	>200	93
Diglycolic acid	100	26	12	8
	330	14	6	6
	660	15	7	7
	1,200	16	7	8
Thiodiglycolic acid	100	----------	37	----------
	330	----------	27	40
	660	71	25	----------

Consideration of the table permits the selection of the acid concentration best suited for stabilizing a particular aqueous hydrogen peroxide solution of determined quality. The stabilizing effect is already appreciable at a concentration of diglycolic or thiodiglycolic acid of 0.05 g./kg. 100% H_2O_2. On the other hand, the use of concentrations greater than 1.5 g./kg. 100% H_2O_2 does not appear to be recommended. The most usual concentration lies between 0.2 and 0.6 g./kg. 100% H_2O_2.

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NOTICE

Nothing contained in this Review shall be construed to constitute a permission or recommendation to practice any invention covered by any patent without a license from the patent owners. Further, neither the author nor the publisher assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process described in this Review.

FERTILIZER INDUSTRIES OF EUROPE 1968

by the British Sulphur Corporation

This book is a guide to the European fertilizer industry. This study describes the pattern of fertilizer production, consumption, and trade, as well as the leading producers in each of the West European countries.

In each of the eighteen West European countries, there is a well established fertilizer industry, producing for local consumption; and in many instances, supplying export markets. Europe is the largest supplier of plant nutrients to overseas consumers. On a world basis, the eighteen European countries account for one-third of total nutrients produced, and one-fourth of total nutrients consumed.

Western Europe is still the dominant factor in the world fertilizer industry. Europe was the birthplace of manufactured chemical fertilizers, over 100 years ago. European industry has had an outstanding record in technical expertise, an intimate knowledge of markets, and agronomic extension work and promotion.

This book is a pertinent summary of the European fertilizer industry, and a valuable work that will be referred to quite frequently.

Describes these Countries:

Austria	Italy
Belgium	Luxembourg
Denmark	Netherlands
Finland	Norway
France	Portugal
Germany	Spain
Greece	Sweden
Iceland	Switzerland
Ireland	United Kingdom

Contains this Information for each Country:

1. General statistics
2. Introduction
3. Fertilizer Production: Production figures for nitrogen, phosphate and potassium; including a discussion of the figures.
4. Fertilizer consumption: Consumption figures for nitrogen, phosphate and potassium; including a discussion of the figures.
5. Fertilizer Exports/Imports: Export and Import figures; including a discussion of the figures.
6. Producers: Names and addresses of the major producers with a discussion of their activities.
7. Graph showing fertilizer consumption and agricultural production from 1962 through 1967.

In addition, the appendix includes a variety of statistical material comparing each European country.

124 pages.

$35

AROMATICS
MANUFACTURE AND DERIVATIVES 1968

by Marshall Sittig

Chemical Process Review No. 17

The market for aromatics in the United States is growing at a rate of about 8% per year, fueled by growth in plastics and fiber production. By 1970 the production of aromatics and derivatives should exceed one billion dollars. By 1970, ninety percent of U.S. aromatics production will be petroleum based.

The vastly increased supply of aromatics which can be separated from catalytic reformates has given the impetus to much of the research as well as industrial applications described here. As paraffinic jet fuels are more desired, aromatic extracts are becoming increasingly available. Thus, the outlook for the future is for increasing supplies of high purity petroleum-derived aromatics as a coproduct of fuel manufacture, and as versatile raw materials for the chemical industry.

The trend in aromatics production and processing is to larger plants with lower production costs. Thus, plentiful production, lower prices, and fast-growing markets, present a favorable picture for the future of aromatic hydrocarbons and their derivatives.

Contains process facts you need: For each process, considerable information is presented under these and other headings:

Feed Materials	Temperature
Pressure	Reaction Time
Reaction Medium	Catalyst
Reactor Design	Product Recovery

The information contained in this Review can be of considerable value to you. Examples of a few of the many processes and illustrations are listed below:

1. Plant for the Isomerization of Pseudocumene to Mesitylene.
2. Apparatus for Feed Preparation for Cyclohexane Manufacture involving Prefractionation.
3. Block Flow Diagram for the Production of High-Impact Polystyrene.
4. Reactor Design for the Production of Dodecylbenzene Sulfonate.
5. Apparatus for the Production of Poly-Para-Xylylene Coatings.
6. Plant for the Production of Hyperpure Benzene by the Hydrodemethylation of Toluene.
7. Integrated Plant for the Production and Recovery of Ethylbenzene.
8. Countercurrent Process for the Separation of Aromatics by Adsorption on Activated Carbon containing Ammonium Fluoride.
9. Clathration Process for Aromatics Separation.
10. Process for Aromatics Recovery from Cracked Gasoline Fractions using Diethylene Glycol Solvent.
11. Process for Aromatics Separation by Extractive Distillation with Dimethylformamide.
12. Process for the Separation of C_8 Aromatics by Distillation.

. . . plus many more.

CONTENTS:

INTRODUCTION

PRODUCTION OF AROMATICS
- By Coking of Coal
- By Coal Hydrogenation
- By Aromatization of Hydrocarbons
- By Combined Coupling and Aromatization

SEPARATION OF AROMATICS
- By Distillation
- By Extractive Distillation
- By Solvent Extraction
- By Crystallization
- By Diffusional Separation
- By Sulfonation
- By Adsorption

PURIFICATION OF AROMATICS
- By Acid Treatment
- By Hydrorefining

REACTIONS GIVING HYDROCARBON PRODUCTS
- Alkylation
- Hydrodealkylation
- Dimerization (Di-p-xylylene manufacture)
- Isomerization

OTHER REACTIONS
- Hydrogenation
- Sulfonation
- Nitration
- Chlorination

PHENOL PRODUCTION
- From Benzoic Acid
- From Chlorobenzene
- From Cumene Hydroperoxide
- From Cyclohexane

STYRENE MANUFACTURE AND DERIVATIVES
- Styrene Monomer
- Polystyrene
- Styrene-Maleic Anhydride Copolymers

FUTURE TRENDS

73 illustrations
232 pages

$35

Noyes Development Corporation— Noyes Building—Park Ridge, New Jersey 07656—U.S.A.
17 Clifford Street, London W. 1, England

TITANIUM DIOXIDE AND TITANIUM TETRACHLORIDE 1968

by Dr. Robert Powell

Chemical Process Review No. 18

Titanium dioxide is the most important white pigment. The history of titanium dioxide manufacture is based on the sulfuric acid process from ilmenite ore. However since 1954, the chlorination process from rutile ore has gradually increased in importance. Today, all new plants are based on the chlorination process, offering better pigment properties, and potentially lower costs.

This book is a technological review of titanium dioxide production processes, based on the chlorination of rutile ore. It describes the various processing steps (a) chlorination of the ore, (b) separation of sublimated solids, (c) purification of crude titanium tetrachloride, and (d) conversion of titanium tetrachloride to titanium dioxide. The outline below shows the various processes described in this book:

INTRODUCTION
- GENERAL
- TITANIUM DIOXIDE
  - Markets
  - Uses
  - Manufacture
  - Economics
  - TiO_2 Statistics

MANUFACTURE OF TITANIUM TETRACHLORIDE
- AMERICAN CYANAMID CO.
  - Recovery of Unreacted Chlorine
- BRITISH TITAN PRODUCTS CO. LTD.
  - Addition of Liquid Tetrachloride Coolant
  - Selective Condensation of Iron Chloride
  - Recovery of Solid Iron Chloride
  - Discharge of Solids
  - Separation of Iron Chloride
  - Maintenance of Uniformly Fluidized Bed
  - Spraying the Chlorinator Gases
  - Improved Chlorine Utilization
  - Chlorination of Material Containing Zircon
- CHAMPION PAPERS, INC.
  - Titanium Tetrachloride and Wood Pulp
- COLUMBIA SOUTHERN (PPG)
  - Chlorination with Hydrogen Chloride
- E. I. DU PONT DE NEMOURS AND CO.
  - Fluidized Bed Reactor
  - Separation of Iron
- FARBENFABRIKEN BAYER
  - Granulation Replaces Briquetting
- ILLINOIS INSTITUTE OF TECHNOLOGY
  - Mixed Process
- MONSANTO
  - Fluidized Bed Chlorination
- MONTECATINI
  - Supplying Heat
- NATIONAL LEAD CO.
  - Flash Chlorination Process
- PITTSBURGH PLATE GLASS CO.
  - Chlorination of Titanium Slag
  - Flame Chlorination
- SHAWINIGAN CHEMICALS LTD.
  - Reaction Heat Electrically Generated
- STAUFFER CHEMICAL CO.
  - From Titanium Carbide
  - Utilization of Titanium Slags
- TEXAS GULF SULPHUR CO.
  - Liquid Sulfur as Suspension Medium

PURIFICATION OF TITANIUM TETRACHLORIDE
- THANN ET DE MULHOUSE
  - Recovery of $TiCl_4$
- LAPORTE TITANIUM LTD.
  - Treatment with Carbonizable Organic
  - Finely Divided Sodium
  - Use of Carbonizable Organic Materials
- NATIONAL DISTILLERS AND CHEMICAL CORP.
  - Treatment with Finely Divided Metals
- PITTSBURGH PLATE GLASS CO.
  - Heating with Sand, Gravel, etc.
- TITANIUM METALS CORPORATION
  - Reaction with Hydrogen
  - Titanium Trichloride
- UNION CARBIDE CORPORATION
  - Carbon Filter Bed

MANUFACTURE OF TITANIUM DIOXIDE
- AMERICAN CYANAMID CO.
  - Water Added Serves as Catalyst
  - Hydrogen Sulfide Acts as Catalyst
  - Using Plasma as Heat Source
- AMERICAN POTASH & CHEMICAL CORP.
  - Eliminate Finishing Operation
- BRITISH TITAN PRODUCTS CO. LTD.
  - Reduce Oxide Deposit
  - $TiCl_4$ with Activated Oxygen
  - Uniform Fluidization
  - Addition of Zirconium Tetrahalide
  - Preheating of Reactants
  - Reduce TiO_2 Accretions
  - Gas Recirculation Method
  - Shaft Furnace
- BRITISH TITAN PRODUCTS CO. LTD./ PITTSBURGH PLATE GLASS CO.
  - Optimization of TiO_2 Particle Size
- CABOT CORPORATION
  - Split Stream Process
  - Hydrolysis Route
  - Reduce Wastage of TiO_2
  - Blanket of Inert Gas
  - Prevent Accumulation of TiO_2
  - Novel Burner Apparatus
- DEGUSSA
  - Special Burner for Hydrolysis
- DOW CHEMICAL CO.
  - Liquid Phase Precipitation Process
- DU PONT
  - TiO_2 in Predetermined Physical Form
  - Inhibit Scale Wall Deposition
  - Eliminate Corrosion
- THANN ET DE MULHOUSE
  - Regulate TiO_2 Particle Size
  - TiO_2 is Continuously Evacuated
- THE GLIDDEN CO.
  - Improved Steam Hydrolysis Process
- LAPORTE TITANIUM LTD.
  - Two Grades of TiO_2 in Single Process
  - Prevent Reactor Blocking
  - Control of TiO_2 Particle Size
  - Minimize Deposition of Oxide
  - Impingement of Inert Material
- PITTSBURGH PLATE GLASS CO.
  - Synergistic Effect
  - Improving Pigment Quality
  - Addition of Metallic Agents
- TITANGESELLSCHAFT M. B. H.
  - Improved Multi-Tube Burner

COMPLETE RECYCLE PROCESSES:
- FROM ORE TO OXIDE
- TITANIUM TETRACHLORIDE VIA THE NITRIDE
  - Metallic Iron as Saleable By-Product
- THE GLIDDEN CO.
  - Chlorination of Ilmenite
  - Hydrochlorination of Ilmenite
- PITTSBURGH PLATE GLASS CO.
  - Combustion of Sulfur-Containing Materials

Numerous illustrations
306 pages

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17 Clifford Street, London W. 1, England

MAN MADE FIBER PROCESSING 1966
by Arthur Alexander
Chemical Process Monograph No. 25

The man-made fiber industry is growing at a rapid rate. By 1970, total U.S. fiber consumption will reach 9 or 10 billion pounds—of which over 50% of tonnage, and over 70% of dollar value will be supplied by man-made fibers.

The contents of this book are largely based upon intelligence gained by "shirt sleeve" experience of the author, currently President of Alexander and Noyes, Inc., Park Ridge, N. J. synthetic fiber consultants.

This book contains a large number of illustrations—flow diagrams, plant layouts, equipment designs, that are of interest to everyone in the industry. There are also a number of tables relating to capital and production costs, and plant equipment lists. Much of this information has never before been published.

Practical processing information is included in these chapters: Rayon, Polynosic, Acetate, Vinal, Vinyon, Acrylic, Polyester, Nylon 66, Nylon 6, Polypropylene, Small Melt Spun Fiber Plants, Monofilaments and Multifilaments, Spandex. 195 pages. **$24.**

STRATEGY FOR PATENT PROFITS 1967
by Roland Dorl

This book embodies a broad investigation into the commercial development and utilization of patents. It explores an apparent gap in modern economic knowledge; namely, just how are patents converted into profit producing assets? With the economic waste of un-utilized or un-profitable patents costing United States industry millions each year, the information here provides useful facts for planning more efficient patent utilization strategy.

Includes comprehensive bibliography. This book is particularly valuable in that it brings together in one place a summary of patent utilization experience.

Chapters: Patents and Their Creation; Trade Secrets, Infringements and Shop Rights; The Licensing and Assignments of Patents; The Difficulties in Marketing a Patent; The Influence of Technological Change on Patent Utilization; Patent Development and Marketing Channels; Methods of Developing a Market for Patents; The Activities of Patent Brokers; Aspects of Patent Economics; Corporations and Their Patent Activity; Case Histories of Patent Utilization; Analysis and Epilog; Bibliography. 138 pages. **$18**

COMBINE HYDROCARBONS AND NITROGEN FOR PROFIT 1967
by Marshall Sittig
Chemical Process Review No. 8

Organic nitrogen chemistry has had a long history, but this field is still in its infancy when placed against the background for future chemical expansion. Nitrogen-containing materials are widely used in fibers, plastics, dyestuffs, drugs, agricultural chemicals, detergents, and high energy fuels.

As huge single-train, 1000 ton-per-day ammonia plants become more numerous and as new nitric acid plants are built, vast quantities of nitrogen raw materials will become more and more available at low cost as building blocks for industrial organic chemicals.

Contents: Introduction, Products From Ammonia, Diethylamine and its Derivatives, Products from Nitric Acid, Alkanolamines and their Derivatives, Pyridine and its Derivatives, Urea Derivatives, Nicotinic Acid and its Derivatives, Products from Calcium Cyanamide, Caprolactam and its Derivatives, Ethylene Imine and its Derivatives, Future Trends 64 illustrations. 200 pages. **$35**

TEXTURED AND NOVELTY YARN PROCESSES 1967
by Mark Harrison

Solve current production problems and develop new products with the help of this book.

In the world today, hundreds of millions of pounds of synthetic fibers are being textured by a wide variety of processes. Yet, for those of you who wish to explore this important subject, there is very little published material. Texturing is a process where cold and slick continuous filament yarns of synthetic fibers are converted into yarns with greatly improved bulk, stretch, adsorbency, and hand.

In this book, Mark Harrison has developed a novel approach in organizing patent information. He breaks it down in a systematic manner, and by using this book, you will be able to research, develop, adapt, and solve problems in this field.

This book has been written so that it is useful to both those well versed in the field, as well as those who have had little experience with these processes, and who want to become more familiar with them. 316 pages and many illustrations. **$35**

COMBINE HYDROCARBONS AND HALOGENS FOR PROFIT 1968
by Marshall Sittig
Chemical Process Review No. 10

This Review is devoted to production processes for the manufacture of large tonnage halogenated organic compounds. Continued, steady growth is expected in this field. In the field of polymers, solvents, refrigerants, pesticides, and organic intermediates, organic halogen compounds play key roles. Expansion in various consuming fields such as coin-operated dry cleaning machines, non-flammable plastics for construction purposes, detergent manufacture, and refrigeration will spur end uses. This Review is primarily concerned with large tonnage chemicals, and therefore emphasis is placed primarily on chlorinated compounds.

Contents: Introduction, Production of Halogenated Methane Derivatives, Production of Halogenated Ethanes and Ethylenes, Production of Halogen Derivatives from Propylene, Production of Halogen Derivatives of Butadiene, Production of Halogen Derivatives of Higher Paraffins, Production of Halogenated Aromatics, Future Trends. 62 illustrations, 181 pages. **$35**

DIBASIC ACIDS AND ANHYDRIDES 1966
by Marshall Sittig
Chemical Process Monograph No. 18

Dibasic acids and anhydrides are among the most important organic chemicals made today. They are essential building blocks for: polyamides for nylon fibers, polyesters for fibers and films, unsaturated alkyd resins for surface coatings, polyester synthetic lubricants, dinitriles, ester plasticizers, and pesticide manufacture.

Detailed process information based on the patent literature for these dibasic acids and anhydrides—oxalic acid, maleic acid and anhydride, fumaric acid, adipic acid, phthalic acids, dimethyl terephthalate, phthalic anhydride, dibasic acids from butadiene, azelaic acid, chlorendic anhydride. Future trends.

Includes many flow diagrams; feed materials temperatures; pressures; reaction times; reaction mediums; catalysts; reactor designs; product recovery. 116 pages. **$20**

CHEMICALS FROM C_4 HYDROCARBONS 1966
by Marshall Sittig
Chemical Process Monograph No. 19

The C_4 hydrocarbons discussed in this book include butane, isobutane, butene and isobutylene. Butane and isobutane are constituents of liquefied petroleum gas (LPG), of which a large portion goes into chemical manufacturing. One of the major refinery byproduct streams is the butane-butene fraction (B-B), generally a mixture of n-butenes, isobutylene, n-butane, and isobutane. The major sources of the butenes are; separation from the B-B fraction, high temperature cracking of naphthas and heavier stocks, and direct dehydrogenation of butane.

Detailed process information based on the patent literature: Oxidation Products; Condensation Products; Alkylation Products; Isomerization Products; Hydration Products; Halogenation Products; Hydroformylation Products; Polmerization Products; Future Trends. 100 pages. **$20**

SYNTHESIS OF ACRYLIC ESTERS BY TRANSESTERIFICATION 1967
by J. K. Haken

Transesterification is a general term for the synthesis of one ester from another. It is a valuable procedure for the preparation of many acrylic esters, but its commercial application has been rather limited, due largely to the lack of readily available information. Transesterification is of more general application than often suggested, and can be utilized for commercial synthesis of many homologous series of esters. With readily available and inexpensive lower esters, the method is attractive even when the equilibrium favors the reactant ester, and the yields of the higher ester are low.

This book also presents the bibliography of available literature, including patents. In this work the patent specifications have been examined, extracted, and tabulated in a common form. The literature of transesterification has been surveyed up through the January 1967 Chemical Abstracts.

J. K. Haken is a Lecturer in Polymer Chemistry at the School of Chemical Technology, the University of New South Wales, Australia. 95 pages. **$18**

SUGAR ESTERS 1968

Important new additives for the food industry.

Already approved for use in foods in a number of countries, use of sugar esters in food in the United States awaits FDA clearance. Sugar esters are an important new raw material for the food industry.

This book contains the papers presented at a Symposium held in California during 1967. The Contents are shown below:

Early History, Nebraska-Snell Process, Present Status of Processes, Sugar Outlook, Use of Sucrose Monopalmitate, Applications in Foods, Animal Feeding, Sucrose Esters in Cosmetics, Sucroglycerides in Foods, The Enhancement of Herbicide Sprays, Herbicide Adjuvants, Effectiveness of Fat-Sugar Derived Surfactants, Laundering Performance, Sucrose Ester Detergents, Evaluation of Sucrose Monotallowates, Water Quality, Water Pollution Problems. 134 pages. **$15**

FLUORINATED HYDROCARBONS AND POLYMERS 1966
by Marshall Sittig
Chemical Process Monograph No. 22

The fluorinated hydrocarbons are now manufactured on a large scale in many parts of the world and have found wide application, in addition to refrigerant uses, as aerosol propellants for insecticides, paints and toilet preparations, and blowing agents for cellular plastics.

The bright future of the fluorochemicals continues to attract new producers which will undoubtedly accelerate process and product research. It will also introduce an increasing degree of price competition which will make the various fluorinated materials more attractive to consumers. Although, the fluorochemicals are high priced products, they possess properties which are unique at any price, and which are essential to space age engineering applications.

Detailed process information is included in these chapters: Fluorinated Methanes; Fluorinated Ethanes; Fluorinated Higher Paroffins; Fluorinated Aromatic Hydrocarbons; Fluorinated Monomers; Fluorinated Polymers; Future Trends. 106 pages. **$20**

OXO PROCESS AND PRODUCTS 1966
by Marshall Sittig
Chemical Process Monograph No. 23

Although industrial emphasis to date has centered predominantly on the synthesis of primary alcohols, the Oxo process is a broadly useful tool which should find much broader application in the future. Just as oxidation and chlorination have been combined into oxychlorination, and just as amination and oxidation have been combined in ammonoxidation, so oxonation may be expected to combine with other unit processes through the use of other hydrogen donors than elemental hydrogen.

Further, increased development effort may be expected to yield processes for the direct synthesis of difunctional compounds as raw materials for films and fibers.

Detailed process information is included in these chapters: Hydrocarbon Synthesis; Aldehyde Manufacture; Aldehyde Dimerization (Aldox Process); Alcohol Manufacture; Glycol Manufacture; Ketone Production; Oxo Products from Unsaturated Esters; Carboxylic Acid Production; Future Trends. 114 pages. **$20**

VINYL MONOMERS AND POLYMERS 1966
by Marshall Sittig
Chemical Process Monograph No. 24

The vinyls are the most important class of plastics and resins. They come very close to holding first place when one considers the vinyl esters alone. When one includes styrene (vinylbenzene), they are by far the most important class.

The vinyls are characterized by the presence of the vinyl group in the monomer molecule. Among the most important of the monomer molecules bearing this vinyl group are: vinyl chloride, vinyl acetate, vinyl cyanide (acrylonitrile), vinyl benzene (styrene); and in most cases these molecules are, or can be, derived from tonnage, low-cost ethylene as the primary hydrocarbon raw material.

Detailed process information is included in chapters devoted to these monomers and their polymers.

Vinyl Chloride; Vinylidene Chloride; Vinyl Formate; Vinyl Acetate; Vinyl Chloracetate; Higher Vinyl Esters; Vinyl Fluoride; Vinylidene Fluoride; Vinyl Ethers; Acrylonitrile; Acrylates; Styrene; Methyl Styrene. 135 pages. **$20**

MIXING IN THE CHEMICAL AND ALLIED INDUSTRIES 1967
by John Randolph

This is a practical down-to-earth book on mixing, based on the patent literature. Mathematical treatment and theory are not included. Included, are solutions for some of the more difficult and troublesome problems in fields ranging from polymer foams to molten metals. Included in this book are some superb summaries of specific technology (i.e. inclusion of carbon black in rubber). An important feature is that the author gives many interesting critical comments and evaluations based on his own long experience.

Mixing of Liquids: Mixing to Produce Foams (Polyurethane), Mixing to Produce Foams (Dough, Bread), Mixing of Viscous Liquids (Epoxies), Mixing of Explosives and Rocket Propellants, Mixing of Polymers, etc., Polymer Finishers and Reactors, Mixing of Viscous Liquids and Plastics, Mixing of Elastomers, Mixing Involving Molten Metals. Blending of Solids: Batch—(Multi-Purpose), Continuous or Batch Blending (Multi-Purpose), Large Capacity—(Resins), Animal Feeds, Abrasives, Rubber. 254 pages. 154 illustrations. **$15**

ORGANIC CHEMICAL PROCESS ENCYCLOPEDIA 1967
by Marshall Sittig

Gives the key processing facts for instant reference for 587 industrial organic chemical processes—with 587 large flow diagrams.

The format of the book is such that the key process facts can be picked out quickly—they are on the same place on every page. Process facts included are: equation; feed materials; coproducts; type of catalyst; phase; reactor type; solvent used; temperature; pressure; reaction time; heat required or heat evolved; product yield; product purity; materials of construction; major product uses; and reference.

The advantage of having all these key facts in one convenient reference source is important to the engineering executive, research director, company executive, market research and development manager, university professor, student, chemical salesman and technical library. 587 pages—8½" x 11"—hard cover. **$35**

LIQUEFIED NATURAL GAS TECHNOLOGY AND ECONOMICS 1967
by C. H. Gatton

The shipment of liquefied natural gas by seagoing tankers was successfully introduced in 1959. Since then, there has been increasing interest in ocean transport of liquefied gases. There appears to be an exciting future for ocean shipment of LNG, ammonia, ethylene, and other gases. Though costs may be high, and competition with naphtha is an important factor, LNG economics are promising for specific applications.

This book gives you broad-spectrum information relating to LNG. Contains many illustrations and tables, as well as a wealth of technical and economic data. Future potentials are also discussed.

Includes these chapters: Liquefied Petroleum Gas, Marine Transportation of LPG, Liquefied Natural Gas, Liquefaction and Revaporization of LNG, LNG Storage, Marine Transportation of LNG, LNG Economics and Future Development, Marine Transportation of Other Liquefied Gases, Bibliography, Appendix—Economics of Sea Transport of LNG. 185 pages. **$15**

SOVIET CHEMICAL INDUSTRY 1967
by Yale L. Meltzer

Although the Soviet Union possesses the second largest chemical industry in the world, very little is known about it outside the Communist-bloc countries. The purpose of this book is to help fill the gap in our knowledge of this important Soviet industry.

Much of the information used to prepare this book was not easily obtained. Much of it was obtained by the author only as a result of his great persistence and patience in weaving together an analysis of the industry.

Trade between the Soviet Union and the West will gradually increase in the future. Soviet authorities realize that help from other countries is necessary to the attainment of their own objectives. This book gives you the basis for understanding the Soviet chemical industry today, so that you can properly plan for future increased trade with the West in chemicals, chemical equipment, and engineering services. 110 pages. **$20**

MEMBRANES TECHNOLOGY AND ECONOMICS 1967
by Dr. Robert Rickles

The membrane process industry will develop into a major business within the next decade, for those firms who can now enter industry on the ground floor.

This book presents both the technical and economic factors that govern the present and future prospects in this fast-growing field. The present status of membranes, equipment and processes are discussed.

A complete summary of those companies which are involved in the industry is presented—together with current and projected economics, and extent of the industry.

This book will assist you in undertaking profitable projects in this field that appears to have a brilliant future.

Chapters: Membrane Theory, Electrodialysis, Ultrafiltration, Dialysis and Diffusion Control, Membrane Filtration, Gas Permeation, Medical Applications, Preparation of Synthetic Polymeric Membranes. 197 pages. **$24**

SYNTHETIC RESINS IN COATINGS 1965
by Harold P. Preuss

This publication surveys the synthetic resins offered for sale by manufacturers in the United States, with particular emphasis on those used in industrial finishes. All told, 49 types of synthetic resins are discussed. For each resin, the following information is given—history, chemistry, properties, manufacturers, specifications, formulation, end use, and application.

An important feature is detailed descriptions for each resin type, of the commercial resins offered by each producer. Gives specific properties, specifications, formulation and application techniques for each proprietary product.

Did you know that as many as 49 different types of synthetic resins are now used in coatings?

This technical/economic/end use study should prove of value to executives in the following functions—research, technical service, marketing, development, and market research. 229 pages. **$12**

POLLUTION CONTROL 1965
by Dr. Robert Rickles

Chemical Process Monograph No. 10

This guide will help you participate in the fast growing pollution control industry. Increasing government regulation, and availability of government funds signifies that this will be a fast growing, profitable industry.

This book attempts to discuss the proven and proposed schemes for solving the problems of pollution control. In each case basic background and practical experience are linked. The markets for chemicals and chemical products are also outlined in each section.

These chapters are included: 1. Introduction, 2. Water Treatment, 3. Water Renovation, 4. Sewage Disposal, 5. Biodegradable Detergents, 6. Solids Disposal, 7. Air Pollution, 8. Radioactive Waste Treatment.

Many flow diagrams and tables are presented. Considerable economic, cost and marketing information is included; in addition to technical details. Future market predictions are included. Pollution control is both a world wide necessity and a business opportunity. 207 pages. **$20**

MARKETING GUIDE TO U.S. GOVERNMENT RESEARCH AND DEVELOPMENT 1966
by Dr. Robert Rickles

The U.S. Government is currently spending about $16 billion per year for research and development. This could rise to $20 billion by 1975. This new book provides a valuable orientation for participation in U. S. government research and development programs.

For each Department, Agency, Division, Authority, Institution, Service, etc., which performs or finances research and /or development in the physical sciences; the following information, where available, has been included: (a) Mission of agency with regard to research and development; (b) Total research and development funds; and extramural research and development funds (order of magnitude); (c) Location of research and development facilities; (d) Officials to contact; (e) Mission of each location; (f) Total research and development personnel; (g) Nature of extramural contracts and restrictions on these contacts; (h) Nature of intramural research; (i) Organizational chart. 229 pages. **$20**

CREATIVE THINKING IN PRACTICE 1966
by Carl Pacifico

A book on creative thinking by Carl Pacifico—a man who has successfully used the techniques outlined in this book, to further the growth of a chemical business.

Emphasis throughout the book is on practical aspects of creative thinking—thoroughly tested for years in the hard competition of industrial life. This is the first book to provide a general understanding of the creative process, together with specific recommendations for building, developing, and implementing those creative thoughts that lead to profits and success.

Chapters: The Concept of Creativity; Understanding the Thinking Process; Keys to Creativity; Techniques for Thinking Creatively; Achieving Creativity; Putting Creativity to Work. 114 pages—hard cover—8½" x 11"—**$9**

PLASTICIZER EVALUATION AND PERFORMANCE 1967
by Ibert Mellan

This book will help you evaluate: 1. A new plasticizer with a known resin; 2. A known plasticizer with an unknown resin; 3. A new plasticizer with a new resin.

The 110 tables of performance data, and the standard methods of testing described in this book, provide data from which one can estimate what a particular plasticizer will do in a specific resin.

The Tables in this book were selected by the author, from manufacturers' literature (at no cost to, nor influence from, the manufacturer of the materials). The plasticizers were chosen for inclusion, primarily by their greatest demand in the industry.

Chapters: 1. Introduction; 2. Testing; 3. Comparative Performance Data; 4. Performance Data of Individual Plasticizers; 5. Brand Names and Their Manufacturers; 6. Abbreviations for Coding Plasticizers; 7. Chemical Names of Plasticizers and Their Brand Names; 8. Brand Names of Plasticizers and Their Chemical Names; 9. Bibliography. 178 pages. **$20**

PLASTIC PIPE 1965
by Dr. C. L. Mantell

Plastic piping is a good growth market for petrochemical products. It is expected that the use of plastic piping in the United States will grow at a rate of 15% per year, twice as fast as the growth of the chemical industry itself.

Includes these chapters: 1. History and Properties, 2. Pipe and Tubing Manufacture, 3. Codes and Engineering Applications, 4. Polyvinyl Chloride, 5. Polyethylene, 6. Specialized Pipe, 7. Abbreviations and Definitions.

For reference, a considerable number of tables are given; the emphasis placed on the competitive situation between plastic and metallic piping, to show the possibilities for replacement.

This volume has been prepared to correlate the existing information on the subject. The growth possibilities for this industry are impressive—there will be continually increasing acceptance for plastic piping under new building codes and standards. 140 pages. **$15**

CORROSION RESISTANT MATERIALS HANDBOOK 1966
by Ibert Mellan

This book helps you cut corrosion costs by using the proper commercially tried and accepted corrosion resistant materials. Most projects involve such a high capital expenditure that only tried and accepted design methods are applicable. 95 Tables selected by the author from manufacturers' literature, (at no cost to, nor influence from, the manufacturer of the materials): Resins (54 Tables); Elastomers (13 Tables); Cements & Mortars (4 Tables); Glass (2 Tables); Wood (4 Tables); Metals & Alloys (18 Tables).

The key to the value of this book is the extensive double indexing. The 95 Tables themselves are arranged by type of corrosion resistant material. The extensive Index is organized by corrosive chemical—and refers you to the specific recommendations in the Tables.

If you have a problem with a corrosive chemical, you will be able to quickly determine the most suitable corrosion resistant material for your requirements. 240 pages. **$25**

EUROPEAN PHARMACEUTICAL MARKET REPORT 1967
by S. A. Mann

This book gives you a pertinent summary of the European Pharmaceutical Industry today.

This book has been prepared to help you obtain a "birds-eye-view" of the European pharmaceutical industry. In most countries outside of the United States, it is difficult to obtain precise market research data. It is hoped that the publication of this report will help you tie together a lot of loose ends, and give you a coherent picture of the European pharmaceutical industry.

Type of information included: General and Historical Background, Foreign Trade, Distribution, Market Structure, Structure of the Industry, Names and Addresses of Major Firms, Growth of the Industry, Prices, Research and Development, Regulations and Development, Health Services.

This book was prepared in our London office. Our London office is a focal point for the gathering of commercial intelligence regarding European processing industries. 111 pages. **$35**

CATALYSTS AND CATALYTIC PROCESSES 1967
by Marshall Sittig
Chemical Process Review No. 7

In this book, catalysts are discussed in terms of the processes which use the catalysts. In each case major emphasis is placed on the catalyst itself—on its composition, preparation and handling in the process. The balance of the process operating conditions are discussed as well, so that the catalyst will be highlighted against a background of discussion of the integrated overall process, including vital catalyst activation and recovery operations, for example.

More and more specific catalysts are being developed to operate on particular molecular species in a feed mixture and to convert them to specific shapes of products. In the past, catalysts used in industry have been of an amorphous nature; however the introduction of molecular sieves has shown the activity of crystalline materials.

Contents: Hydrocarbon Conversion Processes, Hydrocarbon Polymerization Processes, Hydrocarbon Oxidation processes. Future Trends. 109 illustrations. 303 pages. **$35**

PLASTIC FILMS FROM PETROLEUM RAW MATERIALS 1967
by Marshall Sittig
Chemical Process Review No. 6

This Review is devoted to the production of synthetic polymer films. The petroleum-based polyolefins constitute probably the most important single class of plastics today, and high-pressure polyethylene is probably the most important single plastic. Films, in turn, make up the largest single use for such conventional, low-density polyethylene.

In this, as in many fields of chemical product technology, there is a great scarcity of practical information dealing with the materials, equipment, techniques and operating conditions used in actual manufacturing processes. This Review will, it is hoped, begin to overcome that need and will begin, at least, to introduce the reader to the practicalities of polymer manufacture, film production, and film treatment processes.

Contents: Raw Materials, Polymer Manufacture, Film Production Processes, Film Compositions, Film Treating Processes, Future Trends. 118 illustrations. 276 pages. **$35**

INDUSTRIAL GASES MANUFACTURE AND APPLICATIONS 1967
by Marshall Sittig
Chemical Process Review No. 4

Industrial gases is one of the fastest growing areas in our technological economy.

This book discusses conventional cryogenic air separation and purification techniques in considerable detail. Such plants have now reached a high state of refinement as regards low cost, efficient, safe operation. Many of the patents on air separation processes have expired and this opens up opportunities for smaller firms to enter the business.

In order to overcome problems associated with choice of materials of construction, and in refrigeration requirements, engineers and scientists are working on radical new processes, operating at temperatures nearer to room temperature. This book discusses newer techniques such as adsorption using molecular sieves, and permeation using various membrane materials.

This is a down-to-earth practical book summarizing the present state of the art, including all new developments.

313 pages. 103 illustrations. **$35**

STEREO-RUBBER AND OTHER ELASTOMER PROCESSES 1967
by Marshall Sittig
Chemical Process Review No. 3

The synthesis of new polymers having rubber-like elasticity is now a vital and growing industry. The further modification of the molecular architecture of such elastomers to impart specific properties, is the subject of world-wide research. This Review summarizes the present state of the art in the elastomer industry. It covers the field, including new routes to monomers and new polymerization techniques.

This is a down-to-earth, practical book, of value to the elastomer and polymer industry. This Review saves you considerable time and money searching for facts. Marshall Sittig evaluates the pertinent facts in this field.

This book is devoted to manufacturing techniques and processes for stereo and conventional synthetic rubbers. It covers both monomers and polymers. The book is timely and up-to-date. There is more up-to-date commercial process information published in this book on this subject, than has ever been published previously. 215 pages. 77 illustrations. **$35**

POLYOLEFIN PROCESSES 1967
by Marshall Sittig
Chemical Process Review No. 2

This book is devoted to manufacturing techniques and processes for polyolefin resins—from the olefinic feed material to the purified raw material. Thus, it includes catalyst recovery, solvent recovery, and the attendant steps between olefin and polyolefin. This review is based primarily on the patent literature and covers much of the patent art through late 1966. In the United States alone, there is issued an average of three patents a week (150 per year) in this field, highlighting the combination of intense research effort and major commercial potential.

Includes: Current Status of Various Polyolefins, Processes Using Non-Metallic Catalysts, Processes Using Metal Oxide Catalysts, Processes Using Metal Alkyl-Reducible Metal Halide Catalysts, Polymer After-Treatment, Polymer Fabrication, Future Trends.

For each process, data is presented under these headings: Feed Materials, Temperature, Pressure, Reaction Time, Reaction Medium, Catalyst, Reactor Design, Product Recovery. 96 illustrations. 234 pages. **$35**

SYNTHETIC FIBERS FROM PETROLEUM 1967
by Marshall Sittig
Chemical Process Review No. 1

This book discusses production processes and techniques of the four major synthetic fibers of today and tomorrow—nylons, polyesters, acrylics, and polyolefins. The trend in the industry has been to modify fibers specifically for certain uses and then to protect the modification by patents.

Currently, nylon is essentially a billion-pound fiber in the U.S., and accounts for about 50% of synthetic fiber production, both in the U.S. and worldwide. Polyesters are the second most important fibers and they feature the highest rate of growth, about doubling every five years, so that they are expected to hit the billion-pound level in the U.S. by about 1970. Acrylics fall into third place and polyolefin fibers into fourth place.

This process review evaluates technically the synthetic fiber industry. A wealth of processing facts. For each process, data is presented under these headings: Feed Materials, Temperature, Pressure, Reaction Time, Reaction Medium, Catalyst, Reactor Design, Product Recovery. 116 illus. 275 pages. **$35**

OLEFINS-MANUFACTURE AND DERIVATIVES 1968
by Marshall Sittig
Chemical Process Review No. 12

This is a technological review of olefins—manufacture, separation, purification, and reactions. Oriented toward industrial practice, this Review gives you basic information relating to olefins.

This Review concentrates on the olefins which are available or potentially available in large volume. These are the materials of most immediate interest to industry. They are the most rewarding materials from a research standpoint in that development of an interesting end-use will not be hindered by the unavailability of an exotic raw material.

New techniques for producing olefins (such as oxidative dehydrogenation) are the subject of intense research and development, and of increasing commercial application. Dimerization, disproportionation, and polymerization, are all used to tailor available olefin feed materials to commercial requirements for olefins of various chain lengths.

Contents; Introduction, Manufacture of Olefins, Separation of Olefins, Purification of Olefins, Reaction of Olefins. Future Trends. 213 pages. **$35**

ELECTRO-ORGANIC CHEMICAL PROCESSING 1968
by Dr. Charles Mantell
Chemical Process Review No. 14

This volume has been written from the viewpoint of the chemical engineer, with emphasis on plant processes, operating data, and plant design. The commercial successes in this field have been attained by the chemical engineering approach. An important factor in the recent success of electro-organic processes is the much greater variety of engineering materials now available.

Contents: 1. History, Potentials of the Elements, 2. Reaction Potentials and Overvoltage, 3. Controlled Potentials, 4. An Electrolytic Approach to Simple Problems, 5. Electrolytic Amalgams as Reductants, 6. Selectivity of Electroorganic Processing, 7. Experimental Investigation, 8. Engineering Materials for Scaleup, 9. Oxidation and Regeneration of Oxidants, 10. Dialdehyde Starch and Cell Design,11. Oxidation of Sugars, 12. Hydroisomerization, 13. Tetra Alkyl Leads by Electrolysis-Commercial Plant, 14. Electrolytic Treatment of Municipal Water Wastes, 15. Electroplating of Organosols, 18. Future. 186 pages. **$35**

COMBINE HYDROCARBONS AND OXYGEN FOR PROFIT 1968
by Marshall Sittig
Chemical Process Review No. 11

This Review describes the processes for oxidation of hydrocarbons for conversion to profitable products. Recent advances and commercialization of newer techniques have resulted in—a) new direct oxidation routes to propylene oxide from propylene; b) oxydehydrogenation routes to olefins giving higher conversions and higher yields; c) new direct oxidation routes to a variety of carbonyl compounds from hydrocarbon feed materials in single step processes.

This book gives you specific, practical information on oxidation processes such as: Feed Materials, Temperature, Pressure, Reaction Time, Reaction Medium, Catalysts, Reactor Design, Product Recovery.

Contents: Introduction; Cyclic Oxides from Olefins and Diolefins; Acids, Anhydrides and Esters; Olefins and Diolefins by Oxydehydrogenation; Aldehydes and Ketones from Olefins; Alcohols from Paraffins and Cycloparaffins; Peroxy Compounds; Future Trends. 214 pages. **$35**

CHEMICAL GUIDE TO GATT, THE KENNEDY ROUND, AND INTERNATIONAL TRADE 1968
by Yale Meltzer

This book will serve to guide the reader through the intricate labyrinth of intertwining issues connected with the Kennedy Round, the proposed SDR-plan and devaluation of the British pound. These issues cover a vast array of practical R&D, technological, manufacturing, marketing, exporting, importing, financial, corporate, legislative, legal, monetary, fiscal and political problems.

Contents: 1. What is GATT?; 2. The Kennedy Round of GATT Negotiations; 3. The Benzenoid Chemical Industry; 4. A Non-Tariff Barrier to International Trade: American-Selling-Price (ASP) Valuation; 5. Non-Tariff Barriers to International Trade Other Than ASP; 6. The Antidumping Code; 7. Recent Trends in International Trade; 8. Guide to Economic Blocs; 9. Guide to Some Individual Countries and Their Chemical Industries; 10. The Balance-of-Payments, Balance-of-Payments Adjustment, Equilibrium and Disequilibrium; 11. The Eurodollar Market; 12. International Monetary Reform; 13. Future Trends. 379 pages. **$20**

EUROPEAN MAN-MADE FIBER MARKET REPORT 1968
by S. A. Mann

This book will give you an overall picture of the man-made fiber situation in Western Europe. It is a valuable work that will help you in market research studies. Never before has so much statistical information on this subject been included between the covers of one publication.

This report will give you a birds-eye-view of the entire industry, tying together a lot of loose ends, to establish a coherent picture. This book was prepared in our London office. Our London office is a focal point for the gathering of commercial intelligence regarding European processing industries. The tables of end use patterns are particularly valuable to you. For most countries in Western Europe there are no official figures, and these tables represent the best available estimates.

In the chapters discussing individual countries there are numerous tables pertaining to production, consumption, exports and imports. 186 pages. **$35**

PESTICIDE PRODUCTION PROCESSES 1967

by Marshall Sittig

Chemical Process Review No. 5

The pesticide industry in the United States is expected to grow to a one billion dollar industry by 1975, and a two billion dollar industry by 1985 (at manufacturers' price levels). Worldwide growth of pesticides will be even faster, due primarily to rapidly increasing local food production in the developing countries.

This book details specific manufacturing processes for the major commercial pesticides (insecticides, fungicides, and herbicides). Included is such information as: Feed Materials; Temperature; Pressure; Reaction Time; Reaction Medium; Catalysts; Reactor Design; Product Recovery.

Production processes for these pesticides are described: Olefin-based Insecticides; Olefin-based Fungicides; Olefin-based Herbicides; Diolefin-based Insecticides; Diolefin-based Fungicides; Diolefin-based Herbicides; Aromatic-based Insecticides; Aromatic-based Fungicides; Aromatic-based Herbicides. 48 flow diagrams. 200 pages. **$35.**

UREA PROCESS TECHNOLOGY 1968

by Dr. Robert Powell

Chemical Process Review No. 13

A comprehensive up-to-date Review describing urea production processes.

The spectacular rise in urea demand the past five years, has caused numerous advances in urea technology. There are a large variety of processes for urea production, more than most other chemicals. Rapid changes in technology have occurred since 1960, in research, development; and increasing sophistication of production technology, and plant construction techniques.

The information in this book is up-to-date, and is based on information made available since 1960. The information in this volume includes a huge variety of numerical data. Also included are 67 flow diagrams or equipment illustrations. The bibliography contains 142 references.

General Considerations, Processes, Low Biuret Processes, Product Finishing and Controlled Release Fertilizer. 324 pages. **$35**

WOOD CHEMISTRY PROCESS ENGINEERING ASPECTS 1965

by Dr. Motoyoshi Oshima

Chemical Process Monograph No. 11

This new book outlines a new concept of a chemical industry based on wood. The most promising chemical products that can be derived from wood are in the food and polymer fields.

The book deals with products to be obtained from cellulose, hemicellulose, and lignin. It is concerned with the decomposition of wood into hexoses, pentoses, furfural, phenols, etc. and establishing a chemical industry where wood is used as a raw material.

Descriptions of numerous processes are presented. The book is based primarily on German and Japanese technology. Much of this information has never been published in English.

Includes these chapters: 1. Introduction, 2. Wood Hydrolysis, 3. Engineering Discussion of the Saccharification Process, 4. Hexoses and Their Derivatives, 5. Pentoses and Their Derivatives, 6. Lignin.

Includes many flow diagrams, tables, and an extensive bibliography. 157 pages. **$18**

PHOSPHORIC ACID BY THE WET PROCESS 1967

by Robert Noyes

Chemical Process Review No. 9

This book is a practical publication devoted to production of phosphoric acid by the wet process. Production technology is changing rapidly, with new single tank reactors, the advent of superphosphoric acid, new commercial processes for acidulation with hydrochloric and nitric acids, new semihydrate and anhydrite processes, etc. This book describes these as well as conventional processes, in detail.

This book discusses all important production information relating to all phases of wet process phosphoric acid manufacture. In addition, it includes an extensive bibliography of the subject, and numerous illustrations. It should be a valuable reference to those of you associated with the fertilizer and chemical industries.

Contents: Dihydrate Processes, Concentration, Anhydrite and Semihydrate Processes, Acidulation with Other Acids, Superphosphoric Acid Product, Phosphoric Acid Product. Numerous illustrations. 282 pages. **$35**

FERTILIZER DEVELOPMENTS AND TRENDS 1968

by A. V. Slack

This book analyzes the opportunities for improving fertilizer technology based on current world-wide trends in research and development.

A basic assumption of the book is that the reader is familiar with the fertilizer field, and chemistry of fertilizers and current manufacturing methods are discussed only to the extent necessary for adequately relating new departures to standard practice. Moreover, older developments have been included only when necessary for an adequate description of the newer ones—the major emphasis is in departures that have been introduced in the past five or six years, and new developments that will assume major importance in the future.

Contents: Research and Development, Ammonia, Ammonium Nitrate, Urea, Ammonium Sulfate, Slow Release Nitrogen, Other Nitrogen Fertilizers, Phosphoric Acid, Ammonium Phosphate, Nitric Phosphates, Superphosphate, Thermal and Miscellaneous Phosphate Processes, Potassium Fertilizers, Fluid Fertilizers, Bulk Blending, Minor Nutrients. 98 illustrations, 406 pages. **$35**

AMMONIA AND SYNTHESIS GAS 1967

(2nd edition)

by Robert Noyes

Chemical Process Monograph No. 26

This is the second and revised edition of a book originally published in 1964. Since 1964 there have been many significant changes in ammonia technology. This new book is completely revised, based on these newer developments, and contains substantially more information than the earlier work.

The future worldwide growth rate for ammonia will be rapid, since it is the supplier of essentially all fertilizer nitrogen.

This is an up-to-date book outlining technology and economics pertaining to ammonia production, with many flow diagrams, tables, processing numbers and cost estimates. The discussion is organized in reference form, beginning with the various methods of hydrogen and synthesis gas preparation, shift conversion techniques, various carbon dioxide removal systems, final purification, compression, and ammonia synthesis. The bibliography lists 281 references.

Bibliography. Many illustrations. 175 pages. **$20**

NITROGEN FERTILIZER CHEMICAL PROCESSES 1965

by C. J. Pratt and R. Noyes

Chemical Process Monograph No. 4

Contains practical processing information for engineering and management executives. An up-to-date study based on the latest available technical information from the United States, Europe, and Japan.

Every commercial nitrogen fertilizer chemical (except ammonia) is discussed. The chemical processing information for each product is extensive, complete and up-to-date; much comparative information being given on proprietary processes.

Chemical processing details are presented for these fertilizer chemicals: Ammonium Chloride; Ammonium Nitrate; Ammonium Phosphates; Ammonium Sulphate; Ammonium Sulphate Nitrate; Calcium Ammonium Nitrate; Calcium Cyanamide; Calcium Nitrate; Magnesium Ammonium Phosphate; Nitric Acid; Nitrophosphates; Potassium Nitrate; Sodium Nitrate; Urea; Ureaform; Miscellaneous; Recently Developed Products. 250 pages. **$15**

POTASH AND POTASSIUM FERTILIZERS 1966

by Robert Noyes

Chemical Process Monograph No. 15

Much of the book contains process information relating to potash and potassium fertilizers, heavily based on commercial processes from the patent literature. The bibliography of close to 400 references includes 232 pertinent commercially significant U.S. patents. It is the most comprehensive work ever published on the subject. Includes numerous flow diagrams.

Includes These Chapters:
1. Introduction, Markets, Future Projections, 2. Geology and Geography, 3. Underground Deposits of Soluble Minerals, 4. Brines, 5. Other Sources of Potash, 6. Flotation, 7. Crystallization, 8. Other Refining Processes, 9. Potassium Sulphate, 10. Potassium Nitrate, 11. Potassium Phosphates, 12. Final Product.

Considerable marketing information is given, with an estimate of potash consumption in each area of the world for 1970, 1975 and 1980. 210 pages. **$15**

EUROPEAN PETROCHEMICAL FACTS 1968

by Alexander Erdely, Jr.

This survey assembles in one document, essential commercial information on the European petrochemical industry. It is a working reference, in that it allows you to keep up-to-date as future developments are announced, by merely inserting the proper information as it becomes available. It is the most complete summary ever published of the European petrochemical industry. It is indispensable for market research, development, and purchasing.

Contents: Analysis by product; Summary of supply/demand situations and forecasts for basic petrochemicals in Europe; Analysis by country; Summary of major companies and their product lines; Product flow analysis.

For major European petrochemicals it gives plant locations, capacities, processes, feed suppliers, customers, trends, etc. Analyzes three ways—by product, country, and company. 176 pages. **$35**

CONTROLLED RELEASE FERTILIZERS 1968

by Dr. Robert Powell

Chemical Process Review No. 15

Recent development of lower cost processes has stimulated considerable activity in the field of controlled release fertilizers. Because of cost restrictions these products have in the past been used primarily in ornamentals, and as convenience products.

It is expected that controlled release fertilizers should have a wide impact in the area of specialty crops, particularly high value products such as fruits and vegetables. They could also be important for agriculture in tropical and subtropical regions, and in areas of the world where rainfall is heavy.

This book offers you complete technical data on numerous processes and products in this field. The two major approaches are (a) compounds of low solubility, and (b) coated granules.

Introduction; Compounds of Low Solubility, Coated Granules, Prevention of Nitrogen Losses, Rapid-Release Fertilizer. 279 pages. **$35**

DIOLEFINS—MANUFACTURE AND DERIVATIVES 1968

by Marshall Sittig

Chemical Process Review No. 16

Diolefins will assume increasing importance due to new processes, new raw materials, and new products.

Available in huge quantity at low prices as elastomer raw materials, the diolefins do offer attractive possibilities as petrochemical raw materials.

A major avenue of opportunity which has opened for the diolefins in the last few years is polymerization to a slight degree, or oligomerization, to "big-ring" compounds having 8 or 12 carbons atoms in the ring as a result of dimerization or trimerization of butadiene, for example. These materials, themselves olefinic in nature, offer a fantastic range of synthetic possibilities. Hence both the manufacture and utilization of this new family of organic intermediates are covered in some detail in this Review.

Contents, Introduction, Manufacture of Diolefins, Separation of Diolefins, Purification of Diolens, Manufacture of "Big Ring" Compounds, Reactions of Diolefins, Future Trends. 61 illustrations. 197 pages. **$35**

COMPATIBILITY AND SOLUBILITY 1968

by Ibert Mellan

Normally, it requires laborious testing to determine compatibility of polymers, resins, elastomers, plasticizers, and solvents. Predictions made without testing or literature searching, are usually unreliable. However, compatibility and solubility considerations are important. We all know of the many commercial products that were failures, when compatibility and solubility considerations were ignored.

This book helps you evaluate proper materials by the use of 224 tables. The tables were originally published by manufacturers of various materials, and reproduced in this book, to give you a reference work to this important subject. The book contains a wealth of information all conveniently grouped in one format to help save you time and money. The tables are organized in three sections—polymers and resins, plasticizers and esters, and solvents. The tables in each section indicate the solubility and compatibility of the particular material with a wide range of other materials. 304 pages. **$20**

CHEMICAL PROCESS REVIEWS

Chemical Process Reviews are a series of comprehensive up-to-date chemical engineering studies of a particular and well defined area within the overall chemical process and allied industries. In many cases they are industry surveys in themselves. They are written from the *practical processing point of view*, and are of prime interest to managerial, research, development, marketing personnel, etc., in the process industries. Each Review points out economic considerations where pertinent. Each Review includes a considerable number of illustrations.

Synthetic Fibers from Petroleum; Sittig - $35	1967
Polyolefin Processes; Sittig - $35	1967
Stereo-Rubber and Other Elastomer Processes; Sittig - $35	1967
Industrial Gases - Manufacture and Applications; Sittig - $35	1967
Pesticide Production Processes; Sittig - $35	1967
Plastic Films from Petroleum Raw Materials; Sittig - $35	1967
Catalysts and Catalytic Processes; Sittig - $35	1967
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Phosphoric Acid by the Wet Process; Noyes - $35	1967
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Aromatics - Manufacture and Derivatives; Sittig - $35	1968
Paraffins and Cycloparaffins - Manufacture and Derivatives; Sittig - $35	1968
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Acetylene Process and Products; Sittig - $35	1968
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Hydrazine Manufacturing Processes; Powell - $35	1968
Air Pollution Control; Sittig - $35	1968
Water Pollution Control; Sittig - $35	1968
Nitric Acid Technology; Powell - $35	1968
Practical Detergent Manufacture; Sittig - $35	1968
Synthetic Leather from Petroleum; Sittig - $35	1968
Amines, Nitriles, and Isocyanates - Processes and Products; Sittig - $35	1969

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